Universitat de Girona

FORMULACIÓ I CARACTERITZACIÓ DE MATERIALS COMPOSTOS DE POLIPROPILÈ REFORÇAT AMB FIBRES LIGNOCEL·LULÒSIQUES PROCEDENTS DE PODA DE TARONGER. ESTUDI DEL SEU ÚS PER A MATERIALS APLICABLES A LA CONSTRUCCIÓ

Rafel REIXACH COROMINAS

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TESI DOCTORAL

Formulació i caracterització de materials compostos de polipropilè reforçat amb fibres lignocel·lulosiques procedents de poda de taronger. Estudi del seu ús per a materials aplicables a la construcció.

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2015

PROGRAMA DE DOCTORAT EN TECNOLOGIA

Dirigida per: Dr. Xavier Espinach Orús

Dr. Gerard Arbat Pujolràs

Tutor: Dr. Pere Mutjé Pujol

Memòria presentada per optar al títol de doctor per la Universitat de Girona

Universitat de Girona

Dr. Francisco Javier Espinach Orús i el Dr. Gerard Arbat Pujolràs, profesors de la Universitat de Girona,

DECLAREN:

Que el treball titulat “Formulació i caracterització de materials compostos de polipropilè reforçat amb fibres lignocel·lulosiques procedents de poda de taronger. Estudi del seu ús per a materials aplicables a la construcció.”, que presenta el Sr. Rafel Reixach Corominas per a l’obtenció del títol de doctor ha estat realitzat sota la nostra direcció.

I per tal que així consti ho signem,

Dr. Francisco Javier Espinach Orús

Dr. Gerard Arbat Pujolràs

Girona, 9 de juliol de 2015

Utendum est aetate. Cito pede labidur aetes.

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LLISTAT DE PUBLICACIONS

Aquesta tesi es basa en un compendi de les següents publicacions:

Capítol 3:

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ABREVIATURES

σ_t^c: Resistència màxima a tracció de material compòsit (MPa)

σ_t^F: Resistència intrínseca a tracció de la fibra (MPa)

σ_t^{m*}: Aportació equivalent de la matriu en el punt de ruptura (MPa)

σ_f^c: Resistència màxima a flexió de material compòsit (MPa)

σ_f^F: Resistència intrínseca a flexió de la fibra (MPa)

σ_f^{m*}: Aportació equivalent de la matriu en el punt de ruptura (MPa)

V^F: Fracció en volum de reforço sobre material compòsit

V^m: Fracció en volum de la matriu sobre material compòsit

E_t^c: Mòdul a tracció del material compòsit (GPa)

E_t^F: Mòdul intrínsec a tracció de la fibra (GPa)

E_t^m: Mòdul a tracció de la matriu (GPa)

E_f^c: Mòdul a flexió del material compòsit (GPa)

E_t^F: Mòdul intrínsec a flexió de la fibra (GPa)

E_f^m: Mòdul a flexió de la matriu (GPa)

f_c: Factor d'acoblament

χ_1: Factor d'orientació

χ_2: Factor de longitud i interfase

η_e: Factor d'eficiència

η_o: Factor d'orientació

η_l: Factor de longitud

r: Radi de la fibra

d^f: Diàmetre mig de les fibres

l^f: Longitud mitja de les fibres

l_c: Longitud crítica

l_l: Longitud ponderada en longitud de les fibres

l_w: Longitud ponderada en pes de les fibres

v: Coeficient de Poisson

β : Factor model de Hirsch

mROM: Regla modificada de les mescles

FTSF: Factor de resistència a tracció de les fibres

FTMF: Factor de mòdul a tracció de les fibres

FFSF: Factor de resistència a flexió de les fibres

FFMF: Factor de mòdul a flexió de les fibres

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RESUM

Aquesta tesi doctoral i tot el treball experimental s'ha realitzat dintre les línies de treball del grup de recerca, Laboratori d'Enginyeria Paperera i Materials Polímers (LEPAMAP) de l'Escola Politècnica Superior de la Universitat de Girona. Les fibres de reforça amb les que s'ha treballat provenen de la biomassa resultant de la poda de tarongers. Dita biomassa s'ha processat per extreure'n tres tipus de fibres, mecàniques, termomecàniques i químico-termomecàniques. Aquestes fibres s'han usat com a reforç d'una matriu de polipropilè, amb percentatges de fins a un 50% en pes, amb i sense agent compatibilitzador.

En treball consta d'una introducció general on es justifica l'ús de les podes de taronger com a fibres de reforç, tenint en compte l'impacte ambiental d'altres escenaris. De la mateixa manera també s'inclouen els objectius generals de la tesi. Per una altra banda, s'ha cregut convenient introduir una secció amb tots els material, equipaments i mètodes que s'han usat. Encara que aquestes dades estan presents en els articles inclosos, aquest capítol permet introduir observacions que, donades les limitacions d'espai que imposen els articles, no son presents en aquests.

Els articles segueixen el fil conductor de la tesi. Així doncs, en el primer article s'estudia la micromecànica de la interfase entre les fibres i la matriu. L'optimització del percentatge d'agent d'acoblament permet assegurar els valors més elevats de resistència a la tracció, i a la vegada calcular les principals propietats intrínseques de les fibres, respecte a la resistència a la tracció. En el segon article es tracta la evolució de la resistència a la tracció a mida que s'afegeixen fibres de reforç. La evolució lineal de les propietats permeten assumir que la interfase entre les fibres i la matriu és força bona. Les propietats que s'obtenen estan en línia amb les obtingudes amb altres reforços ligno-cel·lulòsics. En el tercer article s'estudia la evolució del mòdul de Young i la seva micromecànica. L'evolució del mòdul també és lineal respecte a la quantitat de fibres de reforç usades. Les propietats micromecàniques i macromecàniques també estan en línia amb la d'altres materials compòsits reforçats amb fibres naturals. En el quart article es realitza un estudi de les propietats tèrmiques dels compòsits ja que en general l'addició de fibres dóna menys estabilitat dimensional que la matriu per si mateixa. La degradació del compòsit es va donar en dues fases diferenciades, la del reforç, prop dels 250ºC i la de la matriu, per sobre dels 340ºC. Per últim, s'exploren les propietats com aïllant sonor dels materials estudiats. Aquest últim article obre les portes a l'ús dels materials en el mon de la construcció, ja que les dades d'aïllament acústic que s'obtenen estan per sobre de les que ofereixen solucions constructives més clàssiques, com els panells de guix.

La tesi mostra les possibilitats dels materials compostos de polipropilè reforçat amb fibres provinents de podes de taronger, essent aquests per una banda presumiblement més sostenibles que els que usen fibra de vidre com a reforç, i per una altra banda valoritza un subproducte agroindustrial, augmentant la cadena de valor agrària, i evitant la seva incineració.

RESUMEN

Esta tesis doctoral y todo el trabajo experimental se ha realizado dentro las líneas de trabajo del grupo de investigación, Laboratorio de Ingeniería Papelera y Materiales Polímeros (LEPAMAP) de la Escuela Politécnica Superior de la Universidad de Girona. Las fibras de refuerza con las que se ha trabajado provienen de la biomasa resultante de la poda de naranjos. Dicha biomasa se ha procesado para extraer tres tipos de fibras, mecánicas, termomecánicas y químico-termomecánicas.

En trabajo consta de una introducción general donde se justifica el uso de las podas de naranjo como fibras de refuerzo, teniendo en cuenta el impacto ambiental de otros escenarios. Del mismo modo también se incluyen los objetivos generales de la tesis. Por otra parte, se ha creído conveniente introducir una sección con todos los materiales, instalaciones y métodos que se han usado. Aunque estos datos están presentes en los artículos incluidos, este capítulo permite introducir observaciones que, dadas las limitaciones de espacio que imponen los artículos, no están presentes en los mismos.

Los artículos siguen el hilo conductor de la tesis. Así pues, en el primer artículo se estudia la micromecánica de la interfase entre las fibras y la matriz. La optimización del porcentaje de agente de acoplamiento permite asegurar los valores más elevados de resistencia a la tracción, a la vez que calcular las principales propiedades intrínsecas de las fibras, con respecto a la resistencia a la tracción. En el segundo artículo se trata la evolución de la resistencia a la tracción a medida que se añaden fibras de refuerzo. La evolución lineal de las propiedades permite asumir que la interfase entre las fibras y la matriz es bastante buena. Las propiedades que se obtienen están en línea con los obtenidos con otros refuerzos ligno-celulósicos. En el tercer artículo se estudia la evolución del módulo de Young y su micromecánica. La evolución del módulo también es lineal respecto a la cantidad de fibras de refuerzo usadas. Las propiedades micromecánicas y macromecàniques también están en línea con la de otros materiales compuestos reforzados con fibras naturales. En el cuarto artículo En el cuarto artículo se realiza un estudio de las propiedades térmicas de los composites ya que en general la adición de fibras da menos estabilidad dimensional que la matriz por sí misma. La degradación del composite se dio en dos fases diferenciadas, la del refuerzo, cerca de los 250ºC y la de la matriz, por encima de los 340ºC. Por último, se exploran las propiedades como aislante sonoro de los materiales estudiados. Este último artículo abre las puertas al uso de los materiales en el mundo de la construcción, ya que los datos de aislamiento acústico que se obtienen están por encima de las que ofrecen soluciones constructivas más clásicas, como los paneles de yeso.

La tesis muestra las posibilidades de los materiales compuestos de polipropileno reforzado con fibras provenientes de podas de naranjo, siendo estos por un lado presumiblemente más sostenibles que los que usan fibra de vidrio como refuerzo, y por otro lado valorizan un subproducto agroindustrial, aumentando cadena de valor agraria, y evitando su incineración.

ABSTRACT

This doctoral thesis and all experimental work have been done within the lines of the research group, Laboratory of Paper Engineering and Polymeric Materials (LEPAMAP) of the Polytechnic School of the University of Girona. The reinforcing fibres used in this study come from the biomass from orange pruning. The biomass has been processed to remove three types of fibres, mechanical, thermomechanical and chemical-thermomechanical.

This work contains a general introduction, where the use of pruning orange as reinforcing fibres is justified, taking into account the environmental impact of different scenarios. Similarly the general objectives of the thesis are also included. Moreover, it has been decided to introduce a section with all materials, equipment and methods that has been used. Although these data are included in articles, this chapter allows to introduce more details, given the space constraints imposed by the research papers.

The research papers follow the thread of the argument. Thus, in the first article micromechanics of the interface between the fibbers and the matrix is studied. Optimization of coupling agent percentage ensures the highest values of tensile strength, while calculating the important intrinsic properties of the fibbers, with respect to the tensile strength. In the second article the evolution of the tensile strength as reinforcing fibbers is added. The linear evolution of the properties can assume that the interface between the fibber and the matrix is quite good. The properties obtained are in line with those obtained with other ligno-cellulosic reinforcements. The third article describes the evolution of Young's modulus and micromechanics are studied. The evolution module is also linear to the amount of reinforcing fibbers used. Micromechanical and micromechanical properties and are also in line with the other composite materials reinforced with natural fibbers. The fourth article there is a study of the thermal properties of composites showing that adding fibber gives less dimensional stability than the matrix itself. The composite degradation occurred in two distinct phases, the reinforcement, near 250ºC and the matrix, above 340ºC. Finally, as sound insulating properties of the materials studied are explored. This last article opens the door to the use of materials in the construction world as soundproofing data obtained are above those offered by more traditional constructive solutions, such as drywall.

The thesis shows the possibilities of polypropylene composites reinforced with fibbers from orange tree pruning, and these by hand presumably more sustainable than those using glass fibber as reinforcement, and secondly an agribusiness valued product, increasing chain land value, and avoiding incineration.

CAPÍTOL I

INTRODUCCIÓ I OBJETIUS

1 INTRODUCCIÓ, ESTRUCTURA Y OBJECTIUS

1.1 Impactes ambientals lligats a la gestió actual de les podes

La poda dels cultius llenyosos és una pràctica del cultiu que es realitza anualment (o bianualment en alguns casos concrets) i que consisteix en la eliminació o reducció de part de les branques del sistema arbori o arbustiu amb la finalitat de formar l'estructura de la planta, el sanejament de plagues i malalties, la regulació de la quantitat de producció i la millorar de la qualitat de la collita (Figura 1) .

Tradicionalment les restes de poda eren utilitzades per l'alimentació del bestiar o bé com a font d'energia (com a combustible d'ús domèstic). Posteriorment, l'aparició de la ramaderia intensiva, l'agricultura industrial i la consolidació de l'ús dels combustibles fòssils han propiciat que la gestió d'una part important d'aquests residus agrícoles consisteixi en la crema de les restes vegetals generades. Aquestes restes vegetals no tenen cap valor productiu i han de ser retirats dels camps de conreu per permetre els treballs posteriors que s'hi han de realitzar.

La crema de residus agrícoles és una pràctica comuna, sobretot en els països en desenvolupament, i genera emissió de gasos contaminants a l'atmosfera (gasos d'efecte hivernacle i també amoníac). No obstant, durant els últims anys, s'ha desenvolupat un conjunt de normatives i reglamentacions referides a aquesta activitat, refusant-la i prohibint-la en molts casos. La seva supressió no només es justifica pel fet de tractar-se d'una pràctica que genera emissions de gasos contaminants, sinó perquè presenta altres perjudicis per al medi ambient com són per exemple la pèrdua de fertilitat del sòl, l'afavoriment de la desertització o l'increment del risc d'incendis.

Figura 1 – Exemple de restes vegetals generades a partir de les tasques de poda en un camp de tarongers.

Actualment la gestió dels subproductes de la poda en cultius llenyosos consisteix bàsicament en la crema de les restes vegetals (Figura 2) o bé en la trituració amb desbrossadores i picadores.

La reutilització de les restes de poda per a produir biomassa o altres productes secundaris es considera actualment una pràctica molt minoritària; únicament se'n té constància en parcel·les experimentals i en alguns estudis.

Figura 2 – Crema de les restes vegetals originades per la poda en un camp de tarongers.

La crema de les restes vegetals, que ens algunes regions és encara una gestió molt estesa, suposa una pèrdua considerable dels nutrients que conté la matèria orgànica (carboni, nitrogen, fòsfor i sofre), a més de les emissions a l'atmosfera de CO^2, gasos d'efecte hivernacle, així com també risc cal considerar el risc d'incendis forestals.

Darrerament hi ha hagut una difusió de la trituració de les restes de poda ja que aquesta pràctica suposa una addició de matèria orgànica que pot repercutir a la millora de paràmetres físics del sòl (K. Kumar & Goh, 2000), i en una reducció de les necessitats de fertilització del cultiu, així com una reducció de les emissions de CO_2 (objectiu del protocol de Kyoto). A més, l'aprofitament de les restes de poda dels conreus està considerada una tècnica bàsica en la producció ecològica i a més, pels seus efectes positius, ha d'estar inclosa en els codis de bones pràctiques agrícoles, essent d'obligat compliment en aquelles finques o explotacions que pretenguin a acollir-se a les subvencions dedicades del Reial Decret 4/2001 sobre mètodes de producció agrària compatible amb el medi ambient.

Tot i aquesta tendència, la necessitat d'haver de disposar de maquinària especial per a poder realitzar aquesta operació i la necessitat d'adaptar les parcel·les a aquest tipus de maneig, juntament amb la baixa rendibilitat agrícola, propicia que la crema de restes vegetals sigui encara avui en dia una pràctica molt estesa.

1.1.1 Alternatives a la gestió actual

Les alternatives a la gestió actual dels productes de la poda passa per la revalorització dels residus agrícoles a partir de la creació de nous materials industrials en el qual la biomassa que s'obté a partir d'aquests subproductes en representa una part important. Per exemple, la inclusió dels residus agrícoles en el desenvolupament de *biocomposites* a partir de Polipropilè reforçat amb fibres procedents de les podes de taronger . En la present tesis es contempla el desenvolupament de

biocomposites amb propietats tècniques d'aïllament acústic, d'aïllament tèrmic, així com una elevada resistència mecànica. Aquests composits podrien ser de gran interès per al sector industrial en els propers anys.

1.1.2 Volum de la poda produïda en cultius llenyosos

A partir de les dades estadístiques de la Comissió Europea, s'han pogut consultar les superfícies agrícoles destinades a cultius llenyosos (*pemanent crops*) de Grècia, Espanya, França, Itàlia, Xipre, Malta i Croàcia (Taula 1).

Taula 1 – Superfícies de cultius llenyosos. Font: Estadístiques de la Unió Europea (Eurostat, 2010)

SUPERFÍCIES CULTIUS (2010) ha					
País	**Fruites**	**Fruits secs**	**Cítrics**	**Olivera**	**Vinya**
Grècia	77.380	31.560	42.770	705.960	86.340
Espanya	231.950	514.540	287.570	2.153.730	852.620
França	143.370	34.410	4.120	17.690	785.650
Itàlia	237.280	176.290	128.920	1.123.330	663.000
Xipre	3.490	3.470	3.760	11.640	7.620
Malta	370	0	110	140	610
Croàcia	20.330	6.670	1.900	17.100	30.330

La figura 3 mostra les dades de producció anual de podes a diferents països de l'arc mediterrani.

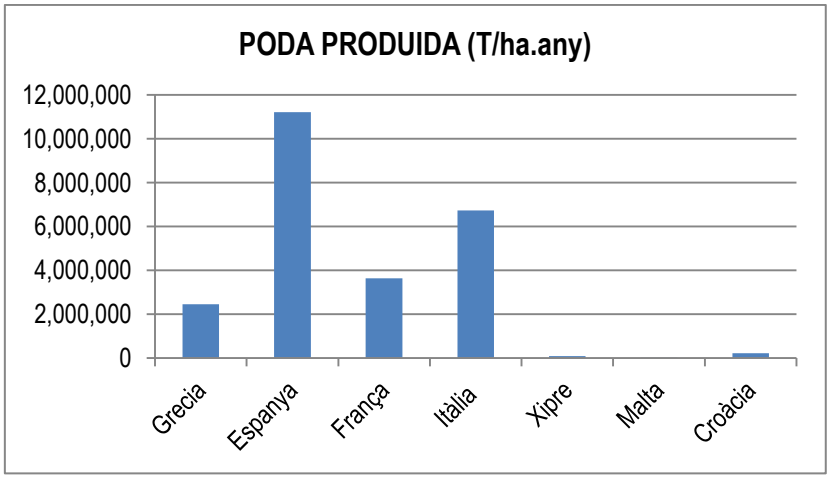

Figura 3 – Superfícies de cultius llenyosos. Font: Elaboració pròpia a partir de les dades estadístiques de la Unió Europea (Eurostat, 2010)

A partir de dades que disposa la Universitat de Girona sobre el rendiment de la poda produïda per superfície (Taula 2), s'ha pogut estimar una quantitat total de restes de poda generada en els cultius llenyosos de tots aquests països (Taula 3). A partir d'aquestes dades es pot estimar, a nivell d'ordre de magnitud, l'impacte i les emissions de CO_2 i altres gasos que afavoreixen l'efecte hivernacle a partir les maneig que es realitza de les restes de poda en conreus llenyosos.

Taula 2 – Factors de conversió per a estimació de la producció de restes vegetals a partir de la poda. Elaboració pròpia segond dades de Ministerio de Agricultura (2012).

Conreu	Poda produïda (T/ha.any)
Fruiters Cítrics	3,7
Fruiters No Cítrics	1,6
Vinya	4,2
Oliveres	2,5
Altres cultius llenyosos	1,6

Taula 3 – Producció de poda procedent de cultius llenyoses. Elaboració pròpia a partir de les dades de (Eurostat, 2010; Ministerio de Agricultura, 2012).

SUBPRODUCTE DE LA PODA (T/ha.any)						
País	Fruites (ha)	Fruits secs	Cítrics	Olivera	Vinya	**TOTAL**
Grècia	123.808	50.496	158.249	1.764.900	362.628	**2.460.081**
Espanya	371.120	823.264	1.064.009	5.384.325	3.581.004	**11.223.722**
França	229.392	55.056	15.244	44.225	3.299.730	**3.643.647**
Itàlia	379.648	282.064	477.004	2.808.325	2.784.600	**6.731.641**
Xipre	5.584	5.552	13.912	29.100	32.004	**86.152**
Malta	592	0	407	350	2.562	**3.911**
Croàcia	32.528	10.672	7.030	42.750	127.386	**220.366**
TOTAL	**1.142.672**	**1.227.104**	**1.735.855**	**10.073.975**	**10.189.914**	**24.369.520**

1.1.3 Identificació, caracterització i avaluació d'impactes

1.1.3.1 Emissions de CO_2

A partir de l'estimació de volum de restes vegetals producte de la poda, es pot estimar la quantitat de diòxid de carboni (CO_2) alliberat a l'atmosfera com a conseqüència de les cremes.

En primer lloc cal considerar que la crema de restes de poda és només un percentatge del total de restes vegetals que es generen, ja que com s'ha comentat anteriorment, una part dels agricultors opten per la trituració en comptes de la crema directa, fracció que té una tendència a augmentar.

Respecte a la fracció de biomassa que finalment es crema, segons el document *Análisis de la incidencia de la supresión de la quema de residuos agrícolas sobre la reducción de emisiones de gases contaminantes en Andalucía* el percentatge és del 78% en oliveres i vinya a la comunitat autònoma d'Andalusia (de Jong et al., 1990). Per a la resta de cultius llenyosos (ametller, taronger, mandariner, llimoner, advocat, albercoquer, cirerer, pruner, pomera, presseguer, nesprer i perer) el document esmentat suposa que la fracció cremada de residus agrícoles és similar al de les oliveres i les vinyes. Com que no es disposen de dades oficials de quin és el percentatge real de la crema de

productes de posa per a la resta de l'estat espanyol, ni tampoc de la resta de països esmentats a l'apartat anterior, s'estima que el percentatge de crema de residus és del 60%. A de Jong et al. (1990) s'indica que per la majoria dels cultius llenyosos tenen un percentatge de matèria seca del 80%.

Coneixent els percentatges de residus que són cremats, i el seu percentatge en matèria seca, finalment només cal realitzar la conversió de tona de fusta a tona de CO_2 alliberat per la combustió. Tal i com es detalla a Carazo (2006) 1 Tm de fusta equival a 1,6 Tm CO_2. Finalment cal tenir en compte un últim factor de conversió, que consisteix en una estimació de la eficiència en el procés de crema de biomassa (la fracció oxidada), que s'estima que és del 90% per a tots els cultius llenyosos (Myhre, Highwood, Shine, & Stordal, 1998).

Aplicant totes aquestes consideracions, s'estima que la quantitat alliberada per la crema de les restes de poda per als diferents cultius llenyosos a Espanya, França, Itàlia, Grècia, Croàcia, Mala i Xipre és de CO_2 alliberats (Figura 4).

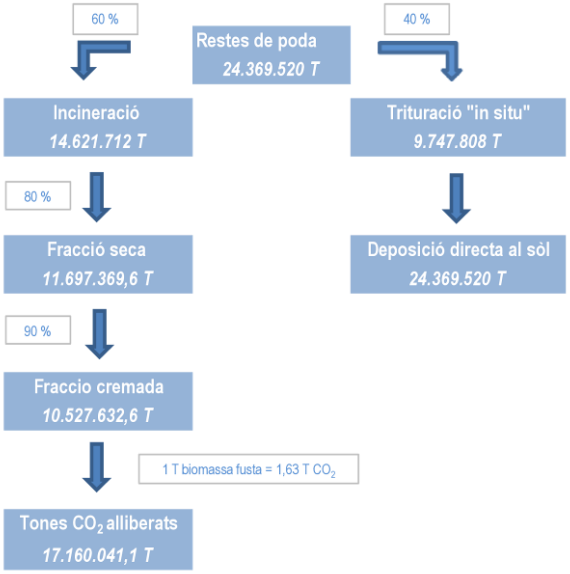

Figura 4: Càlcul del CO_2 generat a partir de les cremes dels residus de la poda en cultius llenyosos. Font: Elaboració pròpia (a partir de les consideracions descrites en aquest mateix apartat).

En tot aquest anàlisi cal tenir en compte una última consideració relatiu al balanç del carboni. I és que es podria considerar que l'emissió a l'atmosfera de CO_2 procedent de la combustió de biomassa té un balanç neutre, ja que amb aquest procés, el CO_2 que s'està alliberant a l'atmosfera és l'equivalent al carboni retingut per la planta durant el procés de creixement i formació d'aquesta mateixa biomassa. L'intercanvi entre el carboni atmosfèric i el de les plantes és un cicle que s'esdevé en un període relativament curt de temps (unes quantes dècades com a molt). Això no passaria amb els combustibles fòssils per exemple, on el que s'està produint és una alliberació de carboni fixat des de fa milions d'anys i que desequilibra el balanç del carboni que s'esdevé en el cicle biomassa – atmosfera.

Un maneig com el que es proposa en el present document, en que la valorització de les restes de poda per part de la indústria implicaria una disminució de les emissions de CO_2 al evitar-se l'eliminació d'aquestes mitjançant les cremes, suposaria un balanç en negatiu (el CO_2 absorbit per la

planta a partir de l'atmosfera no retorna, sinó que continua fixat en un producte industrial), si s'analitza aïlladament el cicle de biomassa-atmosfera. Si es té en compte la descompensació que s'origina a nivell global a causa de la combustió dels combustibles fòssils, es pot considerar aquesta disminució de les emissions de CO_2 a l'atmosfera (per la reducció de les cremes de les restes de poda) té un impacte globalment positiu, considerant que es tracta d'una mesura que ajuda al reequilibri en el balanç global en el cicle del carboni, encara que sigui en un percentatge poc significatiu a nivell global.

1.1.4 Emissions de gasos que afavoreixen l'efecte hivernacle

Un altre aspecte a considerar, a part de les emissions de CO_2, és que la disminució o eradicació de les cremes de les restes de podes en cultius llenyosos implicaria la disminució de les emissions de gasos d'efecte hivernacle que produeix aquesta pràctica. A part dels gasos d'efecte hivernacle, també es reduirien les emissions d'altres gasos que tot i no produir efecte hivernacle, es consideren contaminants (com és el cas del NH_3).

Taula 4 – Càlcul de la fracció de C i N totals a partir de l'estimació del percentatges de cremes dels residus de les podes en cultius llenyosos dels diferents països considerats.

PODA PRODUIDA (T/ha.any)						
País	**Fruites (ha)**	**Fruits secs**	**Cítrics**	**Olivera**	**Vinya**	**TOTAL**
Grècia	123.808,0	50.496,0	158.249,0	1.764.900,0	362.628,0	2.460.081,0
Espanya	371.120,0	823.264,0	1.064.009,0	5.384.325,0	3.581.004,0	11.223.722,0
França	229.392,0	55.056,0	15.244,0	44.225,0	3.299.730,0	3.643.647,0
Itàlia	379.648,0	282.064,0	477.004,0	2.808.325,0	2.784.600,0	6.731.641,0
Xipre	5.584,0	5.552,0	13.912,0	29.100,0	32.004,0	86.152,0
Malta	592,0	0,0	407,0	350,0	2.562,0	3.911,0
Croàcia	32.528,0	10.672,0	7.030,0	42.750,0	127.386,0	220.366,0
TOTAL	**1.142.672,0**	**1.227.104,0**	**1.735.855,0**	**10.073.975,0**	**10.189.914,0**	**24.369.520,0**
80 % de TOTAL FRACCIÓ SECA	914.137,6	981.683,2	1.388.684,0	8.059.180,0	8.151.931,2	19.495.616,0
60 % de FRACCIO SECA CREMADA	548.482,6	589.009,9	833.210,4	4.835.508,0	4.891.158,7	11.697.369,6
90% de COMBUSTIÓ	493.634,3	530.108,9	749.889,4	4.351.957,2	4.402.042,8	10.527.632,6
Fracció C (%)	0,57	0,57	0,55	0,4952	0,57	
Fracció C Total	281.371,6	302.162,1	412.439,1	2.155.089,2	2.509.164,4	*5.660.226,4*
Fracció N (%)	0,0036	0,0036	0,0203	0,0039	0,0036	
Fracció N Total	1.777,1	1.908,4	15.222,8	16.972,6	15.847,4	*49.951,1*

El CO i NOx generats en els conjunt de podes dels països considerats s'especifiquen en les Figura 5 i Figura 6.

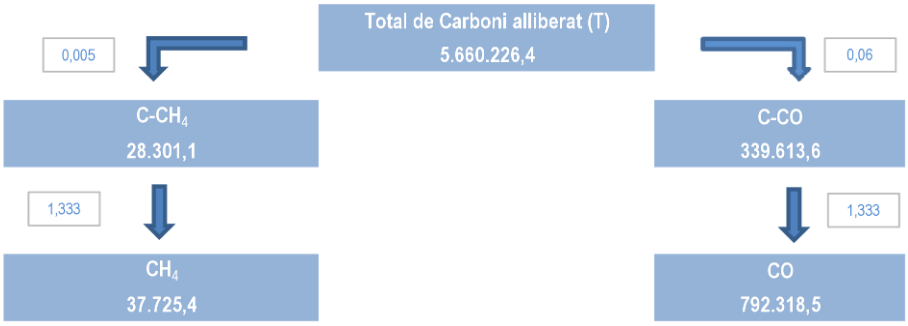

Figura 5– Càlcul del CO generat (tones) a partir de les cremes dels residus de la poda en cultius llenyosos dels diferents països considerats.

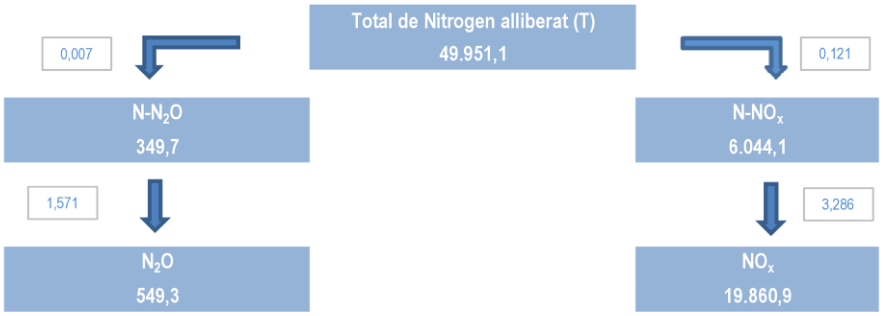

Figura 6– Càlcul del NO_x generat a partir de les cremes dels residus de la poda en cultius llenyosos dels diferents països considerats.

1.1.5 **Resum identificador dels impactes provocats per la crema de podes.**

Taula 5 – **Caracterització dels impactes ambientals de la gestió actual de les restes de poda, i de la gestió alternativa (valorització de les restes de poda).**

MEDI FÍSIC	**Contaminació atmosfèrica**	◎ Les cremes suposen una important font d'emissions de gasos d'efecte hivernacle directes (CH_4 i N_2O) i gasos d'efecte hivernacle indirecte (CO, NO_X, SO_X y $COVNM^2$) i altres gasos contaminants com NH_3. ◎ Hi ha una emissió de gasos derivats de la maquinària durant el procés de triturat de les restes vegetals, en tot cas unes emissions molt menors en comparació a la crema directa. ◎ Hi ha una emissió de gasos derivats de la maquinària durant el procés de transport de les restes vegetals en cas que aquestes siguin transportades a centres de revalorització industrial, en tot cas unes emissions molt menors en comparació a la crema directa.
	Contaminació acústica	◎ Les màquines que trituren les restes vegetals impliquen un augment de soroll en zones rurals, on en general, la sensibilitat acústica és alta segons la legislació vigent (Reial Decret 1367/2007).
	Risc d'incendis	◎ La crema de restes vegetals en els camps de conreu suposen un elevat risc per als incendis forestals. Un percentatge dels incendis forestals originats a l'Estat Espanyol tenen aquests origen). Segons les estadístiques de la Direcció General del Medi Natural de la Generalitat de Catalunya, entre els anys 1994 i 2007 el 13,65% dels incendis forestals originats a Catalunya han tingut el seu origen en les cremes agrícoles.
	Sòls	◎ La crema de restes vegetals impedeix que la reincorporació de macro i micronutrients al sòl, fet que si que pot succeir en part, en el cas de la trituració de restes vegetals. L'aprofitament de les restes vegetals per a la fabricació de productes industrials tampoc permet la reincorporació dels nutrients al sòl. En aquest segon cas, aquests components no es perden per volatilització degut a la combustió de les restes vegetals sinó que simplement es deslocalitza en el producte industrial al qual formarà part, però que tot cas no afavorirà a la fertilització dels sòls agrícoles per la reincorporació dels nutrients però tampoc seran alliberats a l'atmosfera en forma de gas. ◎ La crema de restes vegetals poden afavorir els processos erosius del sòl per l'eliminació de la coberta vegetal en tots aquells punts on es produeixen les cremes.
MEDI BIÒTIC	**Fauna i flora**	◎ El fum i cendres produïts per les cremes de les restes vegetals poden ser activitats que ocasionin molèsties a la fauna salvatge, sobretot si es produeixen a finals d'hivern o principis de primavera, èpoques en que moltes de les espècies inicien el període d'aparellament i cria. ◎ Les cendres o altres productes volàtils de les cremes poden embrutir les fulles de la flora natural propera als camps de conreus, amb pèrdua de la superfície foliar i en conseqüència una reducció de l'eficiència fotosintètica.

	Sanitat vegetal	◎ La crema de restes vegetals pot afavorir a l'eliminació de plagues i malalties dels cultius llenyosos. ◎ En canvi, la trituració de restes vegetals pot no permetre l'eliminació d'algunes plagues i malalties, que poden continuar associades a aquestes restes vegetals i afectar al cultiu durant la campanya següent. L'incidència de plagues i malalties en els conreus afavoreix a un major ús de productes fitosanitaris, un major ús de la maquinària, pèrdua de quantitat i qualitat de la collita, i en conseqüència, una menor rendibilitat agrícola en conjunt. ◎ La revalorització de les restes vegetals per a usos industrials afavoriria a l'eliminació de plagues i malalties ja que la seva retirada dels camps de conreus suposaria, de la mateixa manera que en el cas de les cremes, una operació de sanejament.
MEDI SOCIO-ECONÒMIC	Rendibilitat econòmica	◎ La gestió actual dels productes de la poda suposa una despesa per part de l'agricultor, ja que la crema o la trituració de les restes vegetals suposen importants costos de mà d'obra (en el primer cas) i de maquinària (en el segon cas). Actualment els subproductes de la poda no tenen cap valoració de cap tipus, i es consideren residus que cal gestionar o eliminar de les finques agrícoles.

1.1.6 Valoració del impactes ambientals provocats en la gestió de les podes

La valoració es determinarà qualitativament i en detall per cada aspecte del medi afectat, amb petits matisos i atenent a la següent escala:

IMPACTE COMPATIBLE: Aquell la reversibilitat del qual és immediata després del comiat de l'activitat i no precisa pràctiques protectores o correctores, o les precisa de petita entitat. També s'inclouen aquells que provoquen la pèrdua de factors ambientals que no comporten un canvi en el valor ambiental de l'entorn.

IMPACTE MODERAT: Aquell la recuperació de la qual no precisa pràctiques protectores o correctores massa intensives i en el que la consecució de les condicions ambientals inicials requereix cert temps. També s'inclouen aquells que ocasionen un canvi perceptible en el valor ambiental del conjunt.

IMPACTE SEVER: Aquell en el que la recuperació de les condicions del medi exigeix l'adequació de mesures protectores o correctores i en el que, encara amb aquestes mesures, aquella recuperació precisa un període de temps dilatat. Així mateix s'inclouen aquells que ocasionen la pèrdua d'un valor ambiental notable en el conjunt.

IMPACTE CRÍTIC: Aquell la magnitud del qual és superior al llindar acceptable. Amb el que es produeix una pèrdua permanent de la qualitat de les condicions ambientals, sense possible recuperació, inclòs amb l'adopció de mesures protectores o correctores.

A més a més d'aquestes categories d'impacte, i de cara a la valoració dels impactes positius, s'han establert les següents definicions:

- Impacte **FAVORABLE:** Impacte positiu els efectes dels quals sobre el medi són difícilment quantificables en unitats mesurables, ja sigui pel seu caràcter intangible o per verificar-se els seus efectes a llarg termini (superior a 5 anys). Contarà amb 2 nivells d'intensitat en la valoració quantitativa: Favorable i Molt Favorable.

- Impacte **BENEFICIÓS:** Impacte positiu els efectes del qual sobre el medi són quantificables en algun tipus d'unitat i suposen una millora del medi físic o socioeconòmic tangible a curt termini (1 any) o mig termini (5 anys). Contarà amb 2 nivells d'intensitat en la valoració quantitativa: Beneficiós i Molt Beneficiós.

Taula 6 – Taula resum de valoració dels impactes ambientals de la gestió actual de les restes de poda, i de la gestió alternativa (valorització de les restes de poda).

AVALUACIÓ:	Gestió actual crema dels subproductes de la poda	Gestió actual triturat dels subproductes de la poda	Gestió alternativa revalorització dels subproductes de la poda
Factor del medi			
Medi físic			
Contaminació atmosfèrica	✳✳✳✳	✳✳	✳
Contaminació acústica	✳	✳✳	✳
Risc d'incendis forestals	✳✳/✳✳✳	FAVORABLE	FAVORABLE
Reincorporació de matèria orgànica al sòl	✳	FAVORABLE	✳
Medi biòtic			
Molèsties a la fauna i flora	✳✳	✳✳	✳
Sanitat vegetal	FAVORABLE	✳/✳✳	FAVORABLE
Medi Socioeconòmic			
Rendibilitat de les explotacions agrícoles	✳	✳✳	BENEFICIÒS
Impacte global de l'alternativa	Sever	Moderat	Compatible / beneficiós - favorable

Compatible ✳
Moderat ✳✳
Sever ✳✳✳
Crític ✳✳✳✳

1.1.7 Consideracions finals sobre l'impacte de les diferents opcions considerades en la utilització de les podes per materials bioocomposits

A partir de la identificació i caracterització dels impactes ambientals sobre els principals vectors ambientals analitzats, es conclou que l'alternativa de cremar les restes de poda té un impacte globalment **sever** (Taula 6). El vector atmosfèric és el que en resulta més directament afectat, ja que les emissions de gasos (CO_2, gasos amb efecte hivernacle i altres gasos contaminants) que provoquen les cremes suposen un impacte crític per aquest vector ambiental. L'únic impacte favorable que té aquest tipus de maneig és que és un mètode eficaç per eliminar les plagues i malalties que puguin estar associades a aquestes restes vegetals. En canvi, cremar les restes vegetals suposa un impacte moderat pel que fa al risc d'incendis forestals (el 13,65% dels incendis forestals originats a Catalunya tenen el seu origen en les cremes agrícoles). També es considera que té un impacte moderat sobre la flora i la fauna a causa de les molèsties que el fum i les cendres en suspensió poden ocasionar sobre la fauna i flora natural.

L'altre tipus de gestió que actualment es realitza amb les restes de poda és la trituració de les restes vegetals generades. Aquests alternativa té un impacte ambiental globalment **moderat** (Taula 6). Aquesta alternativa té un impacte compatible pel que fa a les emissions de gasos a l'atmosfera, i aquest és el principal avantatge respecte a la crema de les restes vegetals. Aquesta alternativa té un impacte favorable pel que fa a la reducció del risc d'incendis forestals i també que permet la incorporació de matèria orgànica dins la mateixa parcel·la, la qual implica una aportació de nutrients per al conreu en campanyes posteriors. Així mateix, aquesta pràctica també genera alguns impactes sobre el medi, com la generació de pols i partícules en suspensió o soroll que pot ocasionar molèsties a la fauna i flora salvatge. També pot dificultar l'eliminació de plagues i malalties associades a les restes vegetals, ja que la simple trituració pot ser insuficient per eliminar-les. Finalment, aquesta alternativa implica un cost econòmic, ja que per a realitzar aquest tipus de maneig cal disposar de maquinària específica (picadores o desbrossadores). La crema de restes vegetals no necessita de cap tipus de maquinària especifica però si que requereix de nombroses hores de mà d'obra. En aquests aspecte, el maneig actual de les restes de poda, tant si es cremen com si es trituren, suposen un cost més de la producció i van en detriment de la sempre fràgil rendibilitat agrícola.

L'alternativa plantejada a la gestió que es fa actualment dels subproductes de les podes en cultius llenyosos (la crema i la trituració) consisteix en la recerca i creació de nous materials industrials elaborats totalment o parcialment a partir de la biomassa que es pot obtenir a partir d'aquestes restes vegetals. Per exemple, actualment s'estan estudiant nous materials elaborats amb biomassa i que poden ser de gran interès per a la fabricació de materials *biocomposites* elaborats a partir de biomassa barrejada amb plàstic, amb propietats i funcionalitats que poden ser de gran interès per a diversos sectors de la indústria. L'impacte ambiental de l'alternativa plantejada es valora com a globalment **compatible, favorable i positiva** (Taula 6). La principal diferència respecte al maneig actual (trituració o crema), és que aquesta alternativa implicaria la valorització de les restes vegetals, amb el que deixarien de ser considerades com a un residu que cal eliminar, i passaria a ser un subproducte del qual se'n pot obtenir un profit. Si les restes vegetals es retiressin dels camps de conreu per a ser aprofitades per a la indústria, això comportaria uns impactes favorables, com per exemple la reducció del risc d'incendis forestals i els saneig fitosanitari de les parcel·les (les plagues i

malalties presents a les restes de poda serien retirades). Els impactes sobre els vectors atmosfèric (emissió de gasos) o contaminació acústica serien molt poc rellevants (compatibles). Els components químics de les restes vegetals no serien reincorporats al sòl de la parcel·la (com el cas de la trituració) però tampoc serien alliberats a l'atmosfera (com el cas de les cremes), ja que continuarien fixats a la biomassa però ara formant part d'aquests nous materials industrials. Per tant, el flux de matèria orgànica no es podria considerar, en aquest cas, com una pèrdua irreversible, ja que en funció dels maneig que tinguin aquests biocomposites al final de la seva vida útil, podrien tornar a ser incorporats al sòl, ja que no deixarien de ser materials totalment o parcialment biodegradables.

1.2 **Estructura de la recerca realitzada**

L'estudi anterior deixa clar que l'ús de podes de taronger per a l'obtenció de fibres de reforç representa per una banda una bona solució des d'un punt de vista ambiental, i per una altra banda una valorització d'un subproducte agrari. L'ús del residu de poda per a la fabricació de biocomposits pot suposar una valorització d'aquest residu i també una reducció del cost de fabricació en relació a la utilització d'altres fibres naturals (Mishra & Sain, 2009).

La tesi explora l'ús de la biomassa de podes de taronger com a font de fibres lignocel·lulòsiques que s'usaran com a reforç d'un polímer, en aquest cas polipropilè. L'ús de les fibres naturals en el reforç dels materials compostos termoplàstics té diferents avantatges a part de les mediambientals comentades en l'apartat anterior. Una de les avantatges es que incrementen la seva reciclabilitat en relació a l'ús de fibres més rígides, com la fibra de vidre. A part d'això la baixa densitat de les fibres cel·lulósiques afecta positivament les propietats mecàniques específiques (J. P. López et al., 2012; Reixach, Espinach, et al., 2013).

El reforç de polímers termoplàstics per mitjà de fibres cel·lulòsiques és ara una tecnologia estàndard per millorar les propietats mecàniques com ara el mòdul de Young i la resistència a la tracció de polímers, encara que a costa de la seva ductilitat i resistència a l'impacte (Ku, Wang, Pattarachaiyakoop, & Trada, 2011; V. Kumar, Tyagi, & Sinha, 2011; J.P. López, 2012). Actualment els biocomposits amb fibres naturals s'estan utilitzant en les indústries de la construcció, l'automoció, el packaging i la fabricació de mobles (Julian, Espinach, Verdaguer, Pelach, & Vilaseca, 2012; Fernando Julian et al., 2012; Neagu & Gamstedt, 2007).

Per a realitzar un estudi de la viabilitat tècnica d'aquests materials, el primer pas va ser preparar les fibres. En el primer article de la sèrie: "*Micromechanics of Mechanical, Thermomechanical, and Chemi-Thermomechanical Pulp from Orange Tree Pruning as Polypropylene Reinforcement: A Comparative Study*", es proposen tres mètodes de cocció. La preparació de la poda de taronger per tal d'obtenir una pasta que servirà de reforç del material compòsit es pot fer a partir d'un tractament mecànic (MP), termomecànic (TMP) o químico-termo-mecànic (CTMP), com més agressiu sigui aquest tractament més baix serà el rendiment i per tant es genererant més residus en la preparació de la pasta. Per tant seguin el principi de produir mínim residu en el processat d'un subproducte i veien les propietat de les pastes es treballarà amb els processos amb millors rendiments que són el mecànic i termomecànic. Cada un d'aquests mètodes dóna com a resultat fibres amb diferents aptituds per a la creació de enllaços, principalment de Van der Waals i ponts d'hidrògen entre les fibres i la matriu. De totes maneres, es conegut que les fibres tenen un caràcter hidrofílic, i les matrius hidrofòbic, de manera que la seva interfase acaba sent de mala qualitat. En el

primer article, es proposa l'ús de polipropilè imbricat amb àcid maleic. La evolució de les propietats mecàniques a mida que es va augmentant el percentatge d'agent d'acoblament, donen fe de la bondat d'aquest solució. L'article finalitza amb una anàlisi micromecànica de la interfase. S'usen els models de Hirsch, la regla de les mescles, i les equacions de Kelly i Tyson, juntament amb la solució proposada per Bowyer i Bader. En aquest cas només s'estudien els material reforçats amb un 30% en pes de fibres.

En el segon article:" *Tensile Properties of Polypropylene Composites Reinforced with Mechanical, Thermomechanical, and Chemi-Thermomechanical Pulps from Orange Pruning*", una vegada millorada la interfase respecte la resistència a la tracció, s'estudia la evolució de dita resistència a la tracció a mida que el percentatge de fibres de reforç augmenta. Per a fer-ho es fabriquen materials compostos amb percentatges de fibra de reforç que van d'un 20 a un 50% en pes. El treball mostra com la resistència a la tracció dels materials compòsits creix de forma lineal a mida que augmenta el percentatge de fibres. Aquest indica que la interfase és de bona qualitat. Els resultats són millors per les fibres CTMP, seguides de les TMP i les MP. De totes formes, si es calcula la resistència a tracció relativa al rendiment, el resultat és l'invers. D'aquesta manera, l'article estableix que les fibres MP, amb un rendiment proper al 100% respecte a la biomassa són les que ofereixen unes millors propietats relatives, mentre que les CTMP representen les millors propietats netes. En aquest article també es defineix i s'usa un factor de resistència a tracció de les fibres que permet conèixer l'aportació neta de les fibres a la resistència final del compòsit sense necessitat de conèixer la resistència intrínseca de les fibres.

Una altra propietat important en els materials és la seva rigidesa, o la capacitat de sotmetre's a deformacions sense trencar. Per això, el tercer article:" *Modeling of the tensile moduli of mechanical, thermomechanical, and chemi-thermomechanical pulps from orange tree pruning*" de la sèrie estudia la evolució del mòdul de Young respecte el percentatge de fibres de reforç. En aquest cas, també es constata una evolució lineal de la propietat respecte al percentatge de fibres de reforç. Donat que el mòdul de Young no depèn de la qualitat de la interfase, aquest fet posa de relleu les capacitats de les fibres per rigiditzar els materials compòsits. A més a més, la linealitat de l'evolució de la propietat permet l'ús de models lineals com la regla de les mescles pel mòdul. En aquest cas es va veure que les propietats eren sempre superiors en el cas de les CTMP, seguides de les TMP i de les MP. Es proposa com a justificació d'aquest comportament el major grau de cristal·linitat en el cas dels MP, i el creixement d'aquest grau en augmentar el contingut de fibres. A continuació es modela la micromecànica del mòdul, usant la regla de les mescles i també les equacions de Halpin, Tsai i Pagano. Aquestes últimes inclouen a la seva formulació dades morfològiques de les fibres. Els resultats obtinguts pels dos anàlisis són força semblants.

Un altre problema associat amb l'ús de fibres cel·lulòsiques en materials compostos és la temperatura de processament més baixa a causa de la possibilitat de degradació de les fibres naturals i / o la possibilitat d'emissions volàtils que podrien afectar les propietats mecàniques del composit. Per tal d'evitar aquest problema, l'anàlisi és necessari determinar les propietats tèrmiques dels materials compostos resultats. Aquest anàlisis es presenta en l'article:" *Orange Wood Fiber Reinforced Polypropylene Composites: Thermal Properties*".

Els primers quatre articles permeten caracteritzar mecànicament els materials compostos, i mostren que tenen propietats, en el cas dels compostos amb un 50% de fibres, semblants a les dels

compostos de polipropilè reforçats amb fibra de vidre. Per tant són susceptibles de ser usats en aplicacions semi estructurals. Un dels objectius de la tesi és la cerca d'un ús en construcció dels materials estudiats i una de les possibles aplicacions del material compòsit resultant del polipropilè reforçat amb fibres de poda de taronger és la de panell aïllant que podria representar una alternativa al panell de cartró-guix. Tenint en compte que l'aïllament acústic és una de les característiques més importants d'aquest tipus de panells s'ha fet un estudi acústic del compòsit resultant i s'han comparant amb el material estàndard que seria el cartró-guix. El cinquè i últim article:" *Acoustic properties of agroforestry waste orange pruning fibers reinforced polypropylene composites as an alternative to laminated gypsum boards*", estudia les propietats com aïllants sonor dels compòsits. Els resultats mostren que ofereixen una solució alternativa a les solucions constructives lleugeres usades actualment, oferint a la vegada nivells d'aïllament sonor superiors.

La tesi, per tant, presenta un estudi exhaustiu, partint d'un material que en aquests moments es pot considerar un residu, el valoritza, proposa el seu com reforç, estudia les propietats mecàniques dels materials i finalment proposa un possible ús en construcció.

1.3 **Objectius de la tesi**

Els objectius del present treball són els següents:

1.- Estudiar la capacitat de reforç de fibres de poda de taronger tractades a partir de diferents tractaments: tractament mecànic (MP), termomecànic (TMP) o químico-termo-mecànic (CTMP).

2.- Avaluar l'efecte de l'agent d'acoblament en els compòsits produïts amb MP, TMP i CTMP.

3.- Estimar els paràmetres micromecànics del compòsit (factor d'orientació, resistència al tall interfacial, i resistència intrínseca de les fibres).

4.- Analitzar la potencialitat de valorització del residus de poda de taronger com a reforç de materials compòsits.

5.- Determinar les propietats micro i macromecàniques a tracció dels compòsits de polipropilè reforçats amb diferents percentatges de fibra procedents de les podes de taronger.

6.- Avaluar i modelar el mòdul de Young per a diferents continguts de fibres de reforç

7.- Determinar la temperatura de fusió i de degradació del polipropilè reforçat amb fibres de poda de taronger.

8.- Avaluar el possible ús com a material aïllant del polipropilè reforçat amb fibres de poda de taronger i estudiar les seves qualitats com a aïllant acústic.

CAPÍTOL II

MATERIALS I MÈTODES

2 MATERIALS EQUIPS, MÈTODES, CÀLCULS I MODELITZACIONS

2.1 Materials

2.1.1 Podes de taronger

Les podes de taronger provinents de la poda anual varen ser subministrats amablement per Mas Clara de Domeny (Girona).

2.1.2 Polipropilè

Per preparar els materials compostos es va usar un polipropilè (PP) homopolímer Isplen PP099 G2M fabricat per REPSOL-YPF (Tarragona). Aquest PP te un índex de fluïdesa de 55 g al 10 minuts, a 230ºC i 2.16 kg. La densitat mesurada del polímer és de 0.905 g/cm^3. El seu índex de fluïdesa permet ha de permetre una bona dispersió de les fibres i a la vegada una facilitat de processat dels materials compostos. El PP va ser donat per REPSOL-YPF al grup de recerca LEPAMAP de la Universitat de Girona.

2.1.3 Polipropilè funcionalitzat amb àcid maleic

Per assegurar una bona interfase entre les fibres i la matriu s'usarà polipropilè funcionalitzat amb àcid maleic (MAPP) Epolene G 3015 com agent d'acoplament. Aquest material té un índex d'acidesa de 17.4 mg KOH/g, un pes molecular en pes mig M_w=47.000, i un pes molecular en número mig M_n=24.800. Ha estat subministrat per EASTMAN España S.L.

2.2 Equips

2.2.1 Molí de ganivetes

El moli de ganivetes s'usa per realitzar un classificat inicial de les fibres. La seva funció principal es reduir la mida de les fibres de reforç i individualitzar-les. D'aquesta manera s'assegura una mescla més homogènia entre les fibres i la matriu polimèrica.

El moli ha estat subministrat per AGRIMSA, de Sant Adrià del Besos (Barcelona).

La tolva situada a la part superior del molí s'usa per introduir els materials a la zona de tractament. A l'interior del molí hi ha unes ganivetes axials que donen pas a una zona de tamisat. Els tamisos son variables de manera que es pot triar la mida desitjada de sortida de les fibres individualitzades.

Figura 7: Moli de ganivetes Agrimsa.

1.1.1 Cambra d'assecament

Les fibres de reforç d'origen natural acostumen a tenir un alt contingut d'humitat. D'aquesta manera, anteriorment a la fabricació dels materials compostos, les fibres de reforç son emmagatzemades com a mínim durant 24 hores a 80ºC. Depenent del grau d'humitat desitjat, la estança a la estufa es pot prolongar per més temps.

La estufa usada per la preparació de les fibres es una Dycometal model AFA 288. Usa un circuit tancat de recirculació de l'aire calent. El seu rang de temperatures arriba als 250ºC.

Figura 8: Estufa Dycometal.

2.2.2 **Reactor**

Reactor de tipus únic. Virola amb fondo lleugerament cònic, amb camisa calefactada i agitació.

Esta fabricat amb acer inoxidable AISI 304, assegurant que les fibres tractades no queden contaminades. El reactor té un volum de 50 litres. L'aigua calenta esta controlada mitjançant un PID y una termosonda. L'aigua es calenta mitjançant resistències elèctriques i l'aigua es recircula mitjançant una bomba.

Figura 9: Reactor.

2.2.3 **Desfibrador**

El desfibrador de discos Sprout –Waldron s'usa per desintegrar i individualitzar les fibres. El seu ús permet obtenir fibres individualitzades i per tant amb millor relació d'aspecte.

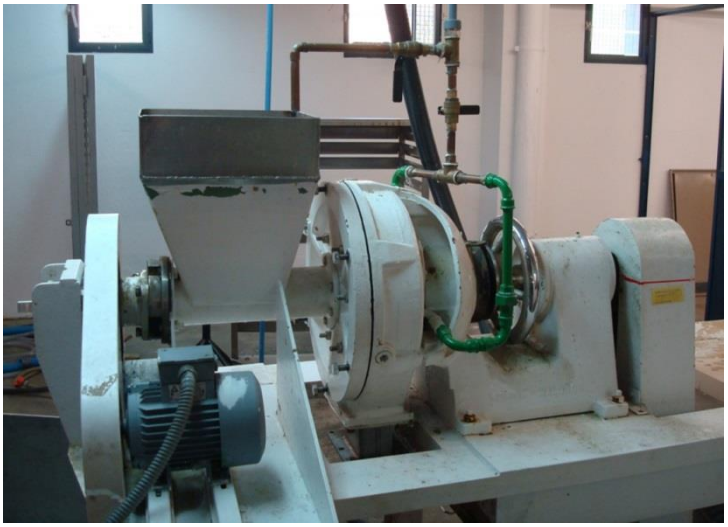

Figura 10: Desfibrador

El detall mostra els discs que s'han usat en el procés de refinat.

Figura 11: Detall ganivetes

2.2.4 **Mescladora interna**

En alguns casos, quan la quantitat de material compost a produir no era molt alta, s'ha usat la mescladora interna Brabender. Aquest aparell permet assegurar una bona dispersió de les fibres dintre la matriu. Durant els procés s'han verificat sempre les corbes de parell y la evolució de la temperatura respecte el temps per assegurar la reproductibilitat dels resultats

Figura 12: Mescladora interna Brabender

2.2.5 **Mescladora multicinètica**

En altres casos, i per produir majors quantitats de compost s'ha usat la mescladora multicinètica Gelimat. Aqueta màquina pot treballar fins a 3000 revolucions per minut, permetent una perfecta dispersió del reforç dintre de la matriu en menor temps. Aquest fet és molt favorable per a les

propietats mecàniques dels materials compostos, ja que per una banda la matriu està sotmesa a una menor degradació tèrmica i les fibres a menors esforços tallants i de fatiga.

Figura 13: Mescladora multicinètica Gelimat

2.2.6 **Plastòmetre**

El plastòmetre és un Melt Flow Quick Index model P/N 7021.000. Està format per una unitat de calefacció elèctrica que controla la temperatura de la zona de sortida del material i a les zones d'alimentació i intermèdia. A l'interior de l'aparell hi ha un cilindre calefactor en el qual s'hi ubica el material a fondre. A l'interior del canal s'hi col·loca, una vegada s'ha dipositat el material, un èmbol al qual s'hi poden aplicar diferents pesos. L'èmbol prem el material contra la sortida. L'índex de fluïdesa mesura el pes de material que surt per la tovera en 10 minuts.

Figura 14: Plastòmetro

2.2.7 **Molí pel·letitzador**

Una vegada s'han barrejar les matrius i les fibres a les mescladores, el molí pel·letitzador s'usa per a fabricar els pellets que s'usaran a la màquina d'injecció. La trituració s'obté mitjançant tres ganivetes situades al rotor de la màquina. El material provinent de les mescladores s'introdueix per la boca superior i els pellets es recullen a la cubeta inferior.

Figura 15: Molí peletitzador

1.1.2 Cambra climàtica

La cambra climàtica és una Dycometal. Té una capacitat de 1m3 y es pot programar per treballar amb un rang de temperatures de -15 a 150ºC, y de 15 a 98% d'humitat relativa. La cambra disposa d'una recirculació forçada d'aire.

Figura 16: Cambra climàtica

1.1.3 Injectora

La màquina injectora és una Mateo & Solé, model Meteor-40. Les característiques tècniques més destacables són:

Pressió màxima d'injecció 1300 kp/cm2, Velocitat màxima d'injecció 45cm3/seg, Potència de calefacció 2,2 kW, Força de tancament 35 MPa y pes injectable màxim 41g.

Figura 17: Maquina injectora amb motlle metàlic

2.2.8 Aparell de mesura universal per assajos a tracció i flexió

Es tracta d'un aparell de mesura que pot tant realitzar assajos a tracció com a flexió canviant els útils. Per a mesurar els mòduls de Young s'ha usat sempre un extensòmetre. És un model Instron 1122.

La màquina disposa d'un sistema informàtic amb tractament integrat de les dades. Les característiques més destacables són:

Capacitat de 5kN, Potència de 500W.

Figura 18: Màquina universal Instron per assajos a tracció i flexió

2.2.9 **Pèndol d'impacte Izod i Charpy**

La mesura de les residències a l'impacte IZOD i Charpy s'han realitzat amb una màquina d'assaig per pèndol. Els diferents tipus d'assaig requereixen un canvi d'utillatges i la realització d'un ranurat o no a les provetes.

2.2.10 **Espectròmetre d'infraroigs**

L'espectròmetre usat és un Matson model Satellite FTIR. L'aparell usa la transformada de Fourier pel processament de les dades. Cobreix l'espectre infraroig.

Figura 19: Espectròmetre d'infraroigs Matson Satellite

2.2.11 **Calorímetre diferencial d'escombrada (DSC)**

Aquest test avalua els processos tèrmics que pot experimentar un material quan es sotmet a proves isotèrmiques a una velocitat constant d'escalfament. Es tracta d'un calorímetre DSC 822 Mettler Toledo, amb una cèl·lula amb sensor ceràmic model ME 27811.

Figura 20: Calorímetre DSC

2.2.12 **Termobalança**

Es tracta d'un equip TGA/SDTA851 Mettler. Es composa d'una balaça d'altra precisió, un forn escalfat per radiació y un termopar.

Figura 21: Termobalança TGA

2.2.13 **Microscopi òptic**

Es tracta d'un Leica model DMR-XA. El microscopi òptic pot augmentar les ostres entre 50 i 1600 augments, amb una reslució de 0,2 µm. El registre de les imatges es realitza mitjançant una càmera Sony.

Figura 22: Microscopi òptic

2.2.14 **Microscopi electrònic d'escombrada**

El microscopi electrònic de rastreig (SEM) usat per realitzar anàlisis morfològics és un Zeiss, model DMS 960, amb una capacitat per realitzar microfotografies de 4 a 300000 augments i una resolució de 25 a 4nm.

Figura 23: Microscopi electrònic

2.2.15 **Aparell Soxhlet**

L'aparell s'usa per extreure les fibres de dintre de la matriu. La matriu es dissolta mitjançant la circulació d'un dissolvent per l'aparell el dissolvent és recuperat i aplicat de nou en recirculació.

Figura 24: Aparell Soxhlet

2.2.16 **Analitzador morfològic**

Els diàmetres i les longituds mitjanes de les fibres extretes dels materials compostos es caracteritzen mitjançant un analitzador morfològic. En aquest cas es tracta d'un MorFi Compact, de Techpap SAS. Com a mínim s'avaluen dues mostres de cada una de les formulacions.

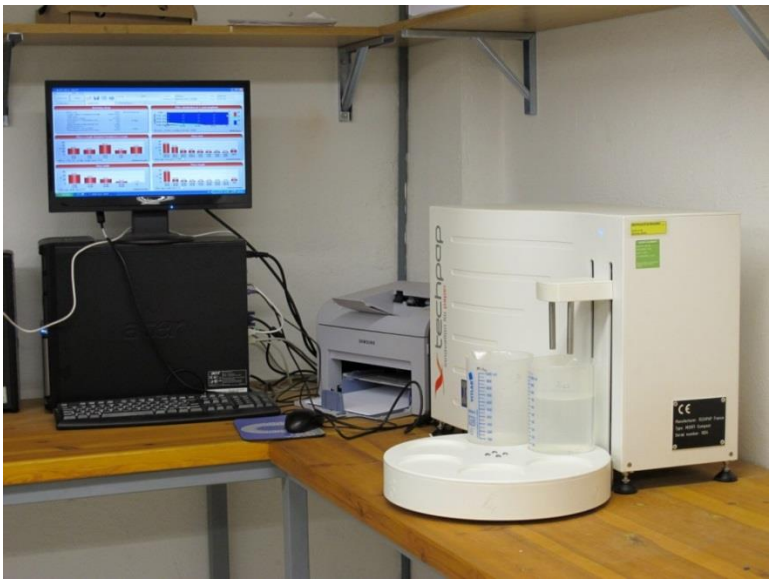

Figura 25: Analitzador MorFi

2.3 **Mètodes**

Es presenten els mètodes més importants que s'han usat a la fase experimental de la recerca. Les publicacions presentades els inclouen però s'ha considerat interessant unificar-les en aquest capítol, com a referència pels lectors.

2.3.1 **Trituració i classificació**

Tota la biomassa de podes de taronger es tracta al molí de ganivetes. Es va usar un tamís de 5mm de diàmetre. D'aquesta manera s'aconsegueixen fibres d'un longitud controlada en comptes de les fibres llargues inicials.

2.3.2 **Preparació de les fibres**

Depenent dels tractaments als que es sotmeten les fibres s'obtindrà pasta mecànica, pasta termomecànica o pasta químico- termomecànica.

Les pastes mecàniques es varen obtenir sotmetent les fibres triturades a un procés de desfibració en fred sota medi aquos. Es va usar el moli Sprout-Waldron y el rendiment final, respecte la biomassa inicial és molt proper al 100%

Les pastes termo-mecàniques es varen obtenir tractant les fibres amb una vaporització seguida de un desfibrat. La vaporització es va realitzar en el reactor, escalfant les fibres a 160 ºC durant 30 minuts. Les fibres obtingudes es varen rentar amb aigua i es varen desfibrar. El rendiment del procés es aproximadament del 95% respecte a la biomassa inicial.

Per obtenir pastes químico-termomecàniques, les fibres tallades varen ser sotmeses a un tractament de cocció amb hidròxid de sodi i antraquinona(AQ) (5% NaOH: 0.1% AQ) en un medi líquid – fibra 4:1, treballant a 160ºC durant 20 minuts. A continuació el resultat es va rentar amb aigua i es va sotmetre a una desfibració. El rendiment equivalent va ser aproximadament del 90%.

2.3.3 **Titulació col·loïdal**

Per la determinació de la polaritat superficial de les fibres s'ha usat la tècnica de la titulació col·loïdal (Carrasco, Mutje, & Pelach, 1996). La tècnica va ser estudiada per primera vegada pel japonès Terayama l'any 1948 (Terayama, 1952).

La tècnica es basa en el fet que la neutralització de la càrrega superficial de la suspensió pot ser neutralitzada mitjançant la adició d'una quantitat equivalent d'un col·loide de càrrega oposada. Els resultats s'expressen en micro equivalents de metil glicol chitosan per gram de reforç o de matriu, depenent del cas.

2.3.4 **Fabricació dels materials compostos**

Els materials compostos, amb percentatges de fibres de reforç que varien del 20 al 50% es varen preparar mitjançant dos mètodes. A la etapa d'optimització del MAPP, es va usar una mescladora Brabender plastograph. Els paràmetres de treball varen ser 80 rpm durant 10 minuts, a una

temperatura de 180 ºC. En el cas de compostos amb MAPP, aquest es va afegir amb els pellets de PP. A la etapa d'estudi de les propietats a tracció, flexió, tèrmiques i d'aïllament acústic, es va usar una mescladora multicinética Gelimat. La mescla es va realitzar a 2500 rpm durant 2 minuts, fins a una temperatura de descarrega de 210ºC.

Els resultats de les mescles es varen triturar al moli de ganivetes per obtenir pellets per a injectar les provetes normalitzades. Una vegada triturades, les mostres varen emmagatzemar-se per 24h a l'estufa. D'aquesta manera s'assegura que no hi ha humitat en el material a injectar.

2.3.5 Mesura de l'índex de fluïdesa

L'equip que es va usar és el plastòmetre. El material es va introduir a la cambra cilíndrica del plastòmetre, a una temperatura de 230ºC. Es va usar un pistó amb una massa de 2.16kg. Es varen fer almenys 3 experiments per a cada formulació. L'índex de fluïdesa s'expressa en grams que han fluid en 10 minuts.

2.3.6 Injecció de les provetes normalitzades

Els pellets de material a injectar es col·loquen a la tolva de la màquina d'injecció. El material es dirigit al cilindre calefactat i transportat mitjançant un cargol sense fi. En el cilindre hi ha diferents zones de temperatura. En aquest cas es distingeixen tres zones a, 175, 175 i 190ºC. El material fos es introduït en un motlle metàl·lic amb cavitats corresponents a les provetes normalitzades per realitzar els test a tracció, flexió, impacte i aïllament sonor.

2.3.7 Condicionament de les provetes

Una vegada injectades, les provetes s'emmagatzemen a una cambra climàtica a 23ºC i una humitat relativa del 50%. Això es fa durant les 48 h anteriors als test normalitzats. Tot això d'acord amb les normes ASTM.

2.3.8 Assaigs a tracció i flexió

Els assaigs a tracció es realitzen en una màquina universal instron. La màquina està dotada d'una cèl·lula de càrrega de 5kN. El el cas de l'anàlisi a tracció, la velocitat del capçal és de 2 mm/min, i es realitzen segons la norma ASTM D638. El mòdul de Young es va obtenir amb un extensòmetre. Els anàlisi a flexió es varen realitzar d'acord amb la norma ASTM D618. Els mode de càrrega és de 3 punts.

2.3.9 Assaigs de resistència a impacte

Els assaig a impacte permeten conèixer el comportament d'un material sotmès a càrregues a una velocitat elevada. Els assaigs es varen realitzar amb entalla i sense. Es varen realitzar assaigs Charpy i Izod. Els assaigs varen complir la norma ISO-180 i ISO 179.

2.3.10 **Extracció de les fibres de l'interior de la matriu**

Les fibres s'extreuen de l'interior de la matriu del compost per avaluar els canvis morfològics que han sofert al llarg del procés de fabricació. Per a fer-ho s'usa un aparell Soxhlet. En el Soxhlet s'evapora un dissolvent que va eliminats la matriu. El dissolvent té un cicle tancat de evaporació condensació. Al final s'obtenen les fibres sense matriu. Les fibres es renten amb aigua i aleshores son susceptibles de ser sotmeses a una anàlisi morfològica.

2.4 **Càlculs i modelitzacions**

Es presenten els càlculs i models més usats en les publicacions

2.4.1 **Càlcul de la fracció en volum dels materials**

La densitat del compost (ρ^c) s'obté de forma experimental seguint la norma ISO 118-3. Aleshores, coneguda la densitat de la matriu (ρ^m), la densitat de les fibres (ρ^f) s'obté de: $\rho^c = w^c/((w^m/\rho^m) + (w^f/\rho^f))$, on w^c, w^m, i w^f son els percentatges en pes del compòsit, la matriu i les fibres. Aillant:

$$\rho^f = \frac{w^f \cdot \rho^m}{\rho^m / \rho^c \cdot \left(w^m + w^f\right) - w^m} \quad (1)$$

Aleshores, la fracció en volum de les fibres es calcula segons:

$$V^f = \frac{w^f \cdot \rho^m}{w^f / \rho^f + w^m / \rho^m} \quad (2)$$

2.4.2 **Càlcul de les longituds compensades i doblement compensades**

Alguns models usen les longituds compensades i doblement compensades. L'anàlisi morfològica de les fibres dona com a resultat una distribució de longituds de fibres, on n_i és el percentatge de fibres que presenten una longitud l_i. Aleshores, la longitud mitja aritmètica (l_a^f) es calcula mitjançant:

$$l_a^f = \frac{\sum_i n_i \cdot l_i}{\sum_i n_i} \quad (3)$$

La longitud compensada en longitud (l_l^f)es calcula mitjançant:

$$l_l^f = \frac{\sum_i n_i \cdot l_i^2}{\sum_i n_i \cdot l_i} \quad (4)$$

I la longitud doblement compensada, o compensada en pes (l_w^f), mitjançant:

$$l_w^f = \frac{\sum_i n_i \cdot l_i^3}{\sum_i n_i \cdot l_i^2}$$

2.4.3 Model de Hirsch

El model de Hirsch (Hirsch, 1962), modela el mòdul de Young dels materials compostos, i es deriva dels models sèrie i paral·lel. La seva formulació és:

$$E_t^C = \beta \cdot \left(E_t^f V^f + E_t^m \left(1 - V^f\right)\right) + \left(1-\beta\right) \frac{E_t^f \cdot E_t^m}{E_t^m \cdot V^f + E_t^f \left(1 - V^f\right)} \quad (5)$$

On β és un paràmetre empíric i que normalment pren un valor de 0.4 pels materials compostos semiorientats reforçats amb fibres curtes. Experimentalment és força fàcil conèixer els mòduls de Young del material compost i de la matriu, de forma que la equació 5 es pot resoldre per obtenir un valor del mòdul intrínsec de les fibres.

2.4.4 Regla modificada de les mescles pel mòdul

La regla modificada de les mescles és un dels models més senzills i elegants que es poden usar per modelitzar el comportament del mòdul de Young dels materials compostos. La seva formulació pels materials semiorientats, reforçats amb fibres curtes és:

$$E_t^C = \eta_e \cdot E_t^f \cdot V^f + E_t^m \cdot (1 - V^f) \quad (6)$$

Aquest model, a diferencia del formulat per a fibres orientades, afegeix un factor d'eficiència (η_e) que compensa els fenòmens deguts a la orientació i longitud de les fibres. El factor d'eficiència es pot expressar com el producte entre el factor d'eficiència de la longitud (η_l) i el d'orientació (η_o).

2.4.5 Model de Cox i Krenchel

El model de Cox i Krenchel (Cox, 1952; Krenchel, 1964) es pot usar per modelar el factor de longitud dels materials compostos. La seva formulació és:

$$\eta_l = 1 - \frac{\tanh\left(\beta \cdot l^f / 2\right)}{\left(\beta \cdot l^f / 2\right)} \quad (7)$$

Amb:

$$\beta = \frac{1}{r} \sqrt{\frac{E_t^m}{E_t^f \cdot (1-\nu) \cdot Ln\sqrt{\pi / 4 \cdot V^f}}} \quad (8)$$

Una vegada calculats els factors d'eficiència i de longitud, serà possible obtenir el factor d'orientació mitjançant:

$$\eta_o = \frac{\eta_e}{\eta_l} \tag{9}$$

2.4.6 **Model de Halpin, Tsai i pagano**

El model de Halpin, Tsai i Pagano (Halpin, 1969; Halpin & Pagano, 1969; Halpin & Tsai, 1969) també es pot usar per modelar el comportament del mòdul de Young dels materials compostos. És un model matemàticament més complex, que afegeix dades morfològiques de les fibres, específicament, la seva longitud mitja (l^f) i el seu diàmetre (d^f). Las seva formulació és:

$$E_t^C = \frac{3}{8}E^{11} + \frac{5}{8}E^{22} \tag{10}$$

On:

$$E^{11} = \frac{1 + 2\left(l^f / d^f\right)\eta_l V^f}{1 - \eta_l V^f} E_t^m \tag{11}$$

$$E^{22} = \frac{1 + 2 \cdot \eta_t V^f}{1 - \eta_t V^f} E_t^m \tag{12}$$

Els paràmetres η_l i η_t venen donats per:

$$\eta_l = \frac{\left(E_t^f / E_t^m\right) - 1}{\left(E_t^f / E_t^m\right) + 2\left(l^f / d^f\right)} \tag{13}$$

$$\eta_t = \frac{\left(E_t^f / E_t^m\right) - 1}{\left(E_t^f / E_t^m\right) + 2} \tag{14}$$

2.4.7 **Regla de les mescles per a la resistència a tracció**

De la mateixa manera que s'usa pel mòdul de Young, hi ha una formulació de la regla de les mescles pel la resistència a tracció dels materials compostos:

$$\sigma_t^C = f_c \cdot \sigma_t^F \cdot V^F + (1 - V^F) \cdot \sigma_t^{m*} \tag{15}$$

A diferencia del mòdul de Young, en aquest cas normalment la fórmula presenta dues incògnites, per una banda el factor d'eficàcia (f_c), que té en compte la pèrdua de propietats del compost degut a la orientació, longitud de les fibres, i la interfase entre les fibres i la matriu. Per una altra banda, normalment, la resistència intrínseca de les fibres no es coneix, i a més a més és complexa i costosa de mesurar experimentalment. El factor d'eficàcia es pot expressar com el producte dels factors d'orientació (f_o) i el de longitud i interfase (f_l).

2.4.8 **Model de Kelly i Tyson**

Kelly i Tyson (Kelly & Tyson, 1965) varen proposar un model per modelitzar el comportament de la resistència a tracció de materials compostos reforçats amb fibres orientades:

$$\sigma_t^C = \sum_i \left[\frac{\tau \cdot l_i^F \cdot V_i^F}{d^F} \right] + \sum_j \left[\sigma_t^F \cdot V_j^F \left(1 - \frac{\sigma_t^F \cdot d^F}{4 \cdot \tau \cdot l_j^F} \right) \right] + (1 - V^F) \cdot \sigma_t^{m*} \quad (16)$$

Aquest model és una reformulació de la regla de les mescles, però agrupa les fibres per longituds, de manera que com més llarga sigui una fibra major serà la seva aportació a la resistència final del material compost. El model divideix les fibres en dues tipologies, les subcrítiques i les supercrítiques. D'aquesta manera, i partint del model shear lag (Tucker & Liang, 1999), es defineix una longitud crítica, a partir de la qual les fibres queden totalment carregades:

$$l_c^F = \frac{d^F \cdot \sigma_t^F}{2\tau} \quad (17)$$

Els diagrames de càrrega seguiran el esquema presentat a la figura 20.

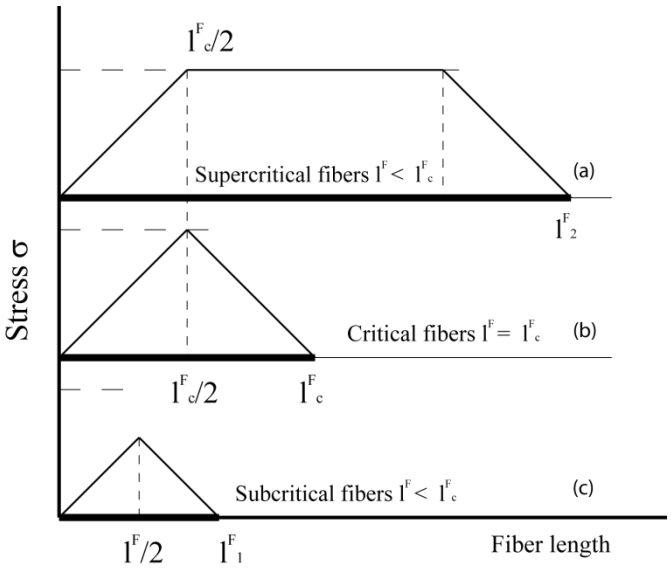

Figura 26: Diagrama de càrrega de les fibres subcrítiques, critiques i supercrítiques (Vallejos et al., 2012)

Per poder usar el model en materials compostos semiorientats es va afegir al model un factor d'orientació (χ_1), essent la formulació de l'equació modificada:

$$\sigma_t^C = \chi_1 \left(\sum_i \left[\frac{\tau \cdot l_i^F \cdot V_i^F}{d^F} \right] + \sum_j \left[\sigma_t^F \cdot V_j^F \left(1 - \frac{\sigma_t^F \cdot d^F}{4 \cdot \tau \cdot l_j^F} \right) \right] \right) + (1 - V^F) \cdot \sigma_t^{m*} \quad (18)$$

2.4.9 **Mètode de Bowyer i Bader**

La equació de Kelli I Tyson presenta normalment 4 incògnites: el factor d'orientació, la resistència intrínseca de les fibres, la tensió interfacial i la longitud crítica. Bowyer i Bader varen presentar una solució a la equació:

$$\sigma_t^C = \chi_1\left(\sum_i\left[\frac{\tau\cdot l_i^F\cdot V_i^F}{d^F}\right]+\sum_j\left[\varepsilon^C\cdot E_t^F\cdot V_j^F\left(1-\frac{\varepsilon^C\cdot E_t^F\cdot d^F}{4\cdot\tau\cdot l_j^F}\right)\right]\right)+(1-V^F)\cdot\sigma_t^{m*} \qquad (19)$$

Aquesta solució suposa, entre altre coses, que la tensió es equivalent a la deformació pel mòdul de Young, i que les fibres i la matriu son sotmeses a la mateixa deformació. La equació 19 es pot expressar com:

$$\sigma_t^C = \chi_1(X+Y)+Z \qquad (20)$$

Si aleshores s'agafen dades experimentals de dos punts, de l'assaig a tracció i es divideixen, s'obté:

$$R=\frac{\sigma_t^{c1}-Z_1}{\sigma_t^{c2}-Z_2};R^*=\frac{\chi_1(X_1+Y_1)}{\chi_1(X_2+Y_2)}=\frac{X_1+Y_1}{X_2+Y_2} \qquad (21)$$

Aleshores, desapareix el factor d'orientació i tenim dues equacions amb dues incògnites. Per mètodes numèrics, i variant el valor de la tensió interfacial es pot arribar a un resultat que compleixi R=R*. Aleshores, aplicant la equació 18, es pot trobar un valor de la resistència intrínseca que avali les dades experimentals.

CAPÍTOL III

PUBLICACIONS

3 MICROMECHANICS OF MECHANICAL, THERMOMECHANICAL, AND CHEMI-THERMOMECHANICAL PULP FROM ORANGE TREE PRUNING AS POLYPROPYLENE REINFORCEMENT: A COMPARATIVE STUDY

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Micromechanics of Mechanical, Thermomechanical, and Chemi-Thermomechanical Pulp from Orange Tree Pruning as Polypropylene Reinforcement: A Comparative Study

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This work explores the use of mechanical (MP), thermomechanical (TMP), and chemi-thermomechanical (CTMP) pulps from orange tree pruning fibers (OPF) as reinforcing elements of polypropylene (PP) composites. Due to the nature of the natural fibers, the use of a coupling agent is needed to attain a good interface and to prevent fiber slippage from the matrix. The main objective of the present work was to investigate the orientation factor, the interfacial shear strength, and the intrinsic strength of the OPF. Coupled and non-coupled composites were formulated and tested, optimizing the coupling agent content with the objective of maximizing the tensile strength of the composites. Hirsch and Kelly-Tyson models and the Bowyer-Bader methodology were used to compute the micromechanic properties. The contribution of subcritical, supercritical fibers, and matrix were also calculated.

Keywords: Orange tree pruning; Mechanical pulp; Thermomechanical pulp; Chemi-thermomechanical pulp; Cationic demand; Interfacial shear strength; Orientation factor; Intrinsic tensile strength

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INTRODUCTION

Environmental awareness has been a popular topic during recent years. An example is the statement of the twelve principles of green chemistry (Anastas and Warner 1998). In regard to composite materials, the main concerns are related to the difficult degradability of plastics, the shortage of landfill space and the increase in the cost of its use, the emissions generated during incinerations, and the increase of cost and decrease of availability of fossil sources. Such considerations have led to interest in the use of fibers obtained from renewable sources as reinforcement for composite materials (Ardanuy *et al.* 2012; Satyanarayana *et al.* 2009). Although there are a lot of potential advantages in favor of that initiative (Satyanarayana *et al.* 2009), there are also some inefficiencies in the interface between natural fibers and polymers to deal with (El Mansouri *et al.* 2012; Vallejos *et al.* 2012).

Tree pruning is a farming practice consisting of removing or shortening some of the branches of the tree in order to facilitate its proper growth, regulate its production,

and improve its quality. Currently, the biomass produced by pruning is usually burned in fields, generating CO_2 emissions and increasing the risk of fire. Spain produces $1.15 \cdot 10^9$ kg/year of citrus pruning residues, which is about 10% of the total produced mass, taking into consideration the main sources of pruning (olive and almond trees, vines, and citrus). The use of orange tree pruning as reinforcement for composite materials can reduce the need for burning, provide low cost alternatives to wood fibers, and extend the value chain for the agricultural industry (Mishra and Sain 2009).

Mechanical pulp from wood fibers is primarily obtained from softwood (Lopez *et al.* 2012a). Although the most common application of that pulp is in the production of printing papers, newsprint, boards, and packaging papers, the MP can also be used as a polymer matrix reinforcing element (Lopez *et al.* 2011, 2012a,b; Mendez *et al.* 2007). On the other hand, depending on the production process and the obtained yield with respect to the raw material, the fibers can also be classified as mechanical pulp (MP), thermo-mechanical pulp (TMP), and chemi-thermomechanical pulp (CTMP). The obtained products are fibers with different physic-chemical properties that can be used as a reinforcing element for composite materials.

The published literature on wood fibers reinforced polymer materials includes several studies on mechanical characterization of the composite materials (Bhattacharyya *et al.* 2003; Lopez *et al.* 2012a; Mendez *et al.* 2007; Zabhizadeh *et al.* 2011). There are also studies on the micromechanics of that kind of composite (Lopez *et al.* 2011, 2012b). Moreover, the influence of the coupling agents on the final mechanical characteristics of the composites has been widely researched (Bhattacharyya *et al.* 2003; Kazayawoko *et al.* 1999; Li and Sain 2003; Nygard *et al.* 2008; Sain *et al.* 2005). Specifically, the literature researching tree pruning as reinforcement for composite materials is scarce and is mainly related to the chemical characteristics of the pulps (Jimenez *et al.* 2004a,b, 2008, 2009; Requejo *et al.* 2012), or manufacture and testing of boards (Cuk *et al.* 2011; Hermawan *et al.* 2009; Pirayesh *et al.* 2011). To the best of our knowledge, there has been research on the production of pulp using OPF (Gonzalez *et al.* 2011), but there is not literature on the use of orange tree pruning fibers (OPF) as reinforcement in PP composites.

In this work, three different processes that generate few byproducts: mechanical, thermomechanical, and chemi-thermomechanical pulping, were tested in order to obtain mechanical pulp (MP), thermomechanical pulp (TMP), and chemi-thermomechanical pulp (CTMP) from orange tree pruning. The produced fibers were morphologically characterized. The breaking length of the fibers was also evaluated according to a paper-making technique. Composite materials were formulated with a 30 wt% of MP, TMP, and CTMP as reinforcement of a polypropylene (PP) matrix. Different percentages of PP and maleated polypropylene (MAPP) were then tested to optimize the percentage of coupling agent in order to obtain the best tensile strength of the composite materials. Once the tensile strength of the composites was maximized, the micromechanic parameters (orientation factor, interfacial shear strength, and intrinsic strength of the fibers) were estimated. Finally, the contribution of the subcritical and supercritical fibers and the matrix to the composite strength were computed. The present research has the aim of providing agroforestry industry with alternatives for the use and valorization of their waste.

EXPERIMENTAL

Materials

The composites were prepared using polypropylene (PP) homopolymer (Isplen PP099 G2M) with an average melt flow rate (230 °C; 2.16kg) of 55 g per 10 min and a density of 0.905 g/cm^3, kindly provided by Repsol-YPF (Tarragona, Spain). Polypropylene functionalized with maleic anhydride (MAH-PP) (Epolene G3015) with an acid number of 15 mg KOH/g and Mn of 24800 Da was acquired from Eastman Chemical Products (San Roque, Spain). Biomass from orange tree pruning fibers (OPF) obtained from seasonal tree pruning was supplied by Mas Clara de Domeny (Girona, catalonia, Spain). Other reactants were used: Diethyleneglycol dimethyl ether (diglyme) was supplied by Clariant and was used as dispersing agent. Decahydronaphthalene (decalin) (190 °C boiling point, 97% purity) supplied by Fisher Scientific was used to dissolve the PP matrix in the fiber extraction from composites process. The reactants that were used for fiber treatment are summarized as follows: sodium hydroxide (Merck KGaA, Darmstadt, Germany), antraquinone (Badische Anilin & Soda Fabric AG, Germany) used without any further purification. Pes-Na (polyethene sodium sulfonate) is an anionic polyelectrolyte. Poly-DADMAC (polydimethyl diallyl ammonium chloride) is a cationic polyelectrolyte. Pes-Na 0.001N and Poly-Dadmac 0.001N were supplied by BTG Instruments GmbH (Germany).

Methods

Preparation of orange tree pruning derivatives

All the biomass from orange tree pruning was submitted to a crushing and classification process. Some OPF samples were submitted to a defibering process under cold aqueous conditions in a Sprout-Waldron equipment to obtain mechanical pulp (MP) with a higher aspect ratio. This process gave almost 100% yield with respect to the starting material (Ashori and Nourbakhsh 2009; Thamae *et al.* 2008). Another OPF sample was submitted to a thermo-mechanical process (vaporization followed by defibering). The OPF were heated to 160 °C for 30 min, and the obtained pulp was rinsed with water and then passed through Sprout-Waldron equipment, resulting in thermo-mechanical pulp (TMP) with an increased reactant surface, and around 95% yield. For OPF chemi-thermomechanical fibers, the OPF were submitted to a sodium/ hydroxide/antraquinone (AQ) cooking process (5% NaOH: 0.1% AQ) in a liquid to fiber ratio of 4:1, working at 160 °C for 20 min. Afterwards, the slurry was washed and shredded in Sprout-Waldron equipment, giving around 90% yield.

Preparation of paper handsheets for mechanical testing (papermaking route)

The handsheets for mechanical testing were prepared in a sheet former (ISP mod. 786 FH). Handsheets were made according to ISO 5269-2 and conditioned in a weather chamber at 25 °C and 50% humidity for 48 h before mechanical testing.

Tensile Strength (TS)

Testing experiments were performed in a Housfield 42 universal testing machine, equipped with a 2.5 kN load cell. Testing was performed according to ISO standards 1924-2. The gap between clamping jaws was set to 150 mm, and the cross head speed was set to 20 mm/min. Preload was set at 2 N. Testing specimens were cut into paper strips 15 mm in width and 210 mm in length.

Density measurement

The density measurement of the composite (ρ^c) was carried out using a pycnometer. Distilled water was used as a reference liquid at 23 °C. The ISO 118-3 standard was respected throughout this experiment. The density of the fiber (ρ^f) was obtained from: $\rho^c = w^c / ((w^m/\rho^m) + (w^f/\rho^f))$, where, were w^c, w^m, and w^f are the loads in weight of the composite, matrix, and fiber, and ρ^m is the density of the matrix.

Evaluation of the cationic demand

The cationic demand of the pulp suspension was determined with a streaming current detector, the Mütek (TM) Particle Charge Detector PCD-04 from BTG Instruments BmbH, (Germany). The streaming current method was used to detect the endpoint of a polyelectrolyte titration, which is related to the colloidal titration technique developed by Terayama (1952). The colloidal titration technique determines the polymer concentration added in excess in the supernatant. The weight of the cationic polymer adsorbed versus the dry weight of the sample in the suspension was calculated by measuring the difference with respect to the initial amount added (Carrasco *et al.* 1996; Rouger and Mutje 1984).

Compounding

Composite materials comprising 30 wt% PP/OPF with and without coupling agent were obtained. The materials were prepared in a Brabender® plastograph internal mixing machine. The working parameters were 80 rpm for OPF during 10 min at a temperature of 180 °C. In the case of the coupled composites, the MAH-PP was added to the plastograph with the PP pellets. The resulting blends were ground with a knives mill, dried, and stored at 80 °C for at least 24 h before processing.

Composite processing

The samples for the tensile test were produced with a steel mould in an injection-molding machine (Meteor 40, Mateu & Solé). Ten test specimens from each obtained composite blend were used for the experiment. The processing temperatures were 175, 175, and 190 °C (the machine has three heating areas), the last corresponding to the injection nozzle. First and second pressures were 120 and 37.5 kgf/cm^2, respectively. Standard composite specimen samples (approx. 160 x 13.3 x 3.2 mm) were obtained and used to measure the tensile properties in agreement with ASTM D638.

Mechanical characterization

Prior to the mechanical testing, the specimens were stored in a Dycometal conditioning chamber at 23 °C and 50% relative humidity for 48 h, in agreement with the ASTM D638 standard. Afterwards, composites were assayed in a Universal testing machine (Instron™ 1122), fitted with a 5 kN load cell and operating at a rate of 2 mm/min. Tensile properties were analyzed by means of dog-bone specimens, according to the ASTM D638 standard. Results were obtained from the average of at least 5 samples.

Fiber extraction from composites

Reinforcing fibers were extracted from composites by matrix solubilization using a Soxhlet apparatus and decalin as solvent. Small pieces of composites were cut and

placed inside a cellulose filter and set into the Soxhelt equipment. A small cotton tab was used to prevent the fibers from getting out of the filtering tube. The fiber extraction was completed after 24 h. Once the fibers were extracted, they were rinsed with acetone and then with distilled water in order to remove the solvent residue. Finally the fibers were dried in an oven at 105 °C for 24 h.

Determination of the fiber length and diameter

Fiber's length distribution and diameter of the extracted fibers were characterized by means of a MorFi Compact (Morfological fiber analyser), from Techpap SAS, (France). A minimum of two samples were analyzed.

Determination of Young's moduli of the fibers

The intrinsic tensile moduli of the MP, TMP, and CTMP from citrus pruning wood fibers were determined using the Hirsch model (Hirsch 1962; Lopez *et al.* 2011; Rodriguez *et al.* 2010; Vilaseca *et al.* 2010).

Determination of the interfacial shear strength (τ) and the fiber orientation factor (χ_1)

With current standard processing techniques, perfect fiber alignment is almost impossible, and the orientation factor (χ_1) must be taken in account. The calculation of τ can be accomplished through the Kelly-Tyson modified equation (Eq.1) (Kelly and Tyson 1965; Lopez *et al.* 2011; Rodriguez *et al.* 2010; Thomason 2002; Vallejos *et al.* 2012).

$$\sigma_t^C = \chi_1 \left(\sum_i \left[\frac{\tau \cdot l_i^f \cdot V_i^f}{d^f} \right] + \sum_j \left[\sigma_t^f \cdot V_j^f \left(1 - \frac{\sigma_t^f \cdot d^f}{4 \cdot \tau \cdot l_j^f} \right) \right] \right) + (1 - V^f) \cdot \sigma_t^{m*} \qquad (1)$$

In Equation 1, σ_t^C and σ_t^f represent the ultimate tensile strength of the composite and the reinforcing fibers. The σ_t^{m*} term is the contribution of the matrix at failure. The d^f and $l_{i,j}^f$ terms represent the fiber diameter and length, respectively. The V^f term is the volume fraction of reinforcement in the composite. In order to solve the equation, the Bowyer–Bader methodology was used (Bowyer and Bader 1972) evaluating χ_1 and τ.

Determination of the intrinsic tensile strength (σ_t^f)

Once the intrinsic tensile modulus, τ, and χ_1, were known, the intrinsic tensile strength was calculated applying the data for the ultimate failure point in Eq. 1. The Bowyer-Bader model, as an approximation, involves the following assumptions: that the stress transfer at the interface increases linearly from zero at the fiber end to a maximum value; that fiber-matrix debonding does not happen; that χ_1 is independent of strain and constant for all fiber lengths; that interfacial shear stress is independent of loading angle; that porosity in the composite is negligible; and that fiber and matrix stress *vs.* strain curves are linear (Li *et al.* 2009; Lopez *et al.* 2011; Rodriguez *et al.* 2010; Vallejos *et al.* 2012).

RESULTS AND DISCUSSION

The tensile properties of a composite material usually depend on the nature of the reinforcement and the polymeric matrix, the dispersion grade of the reinforcement into the matrix, the aspect ratio of the reinforcement (ratio between length and diameter of the fibers l/d), the orientation of the fibers inside the composite, and the quality of the interface between the fibers and the matrix (Lopez *et al.* 2011; Thomason 2002; Vallejos *et al.* 2012; Vilaseca *et al.* 2010).

Nature of the reinforcement fibers

Table 1 shows the pulp and fiber parameters that can have significant influence on the competitiveness of composites. *Yield* refers to the ratio between dry raw material and processed matter, *TS* is the tensile strength of the paper sheet, *pDADMAC* evaluates the cationic demand of the fibers surface and is measured in microequivalents of polyDADMAC per gram of reinforcement, l_w^f and d^f are the mean weighted length and diameters of the fibers, *and* l_w^f / d^F is known as the aspect ratio.

Table 1. Pulps Experimental Parameters

	Yield (%)	*TS* (MPa)	*pDADMAC* (μeq/g)	l_w^f (μm)	d^f (μm)	l_w^f / d^f
MP	99.1	4.81	92.52	331	18.95	17.5
TMP	94.7	11.61	90.50	489	18.15	26.9
CTMP	90.1	13.80	88.06	485	18.70	25.9

In agreement with the principles of green chemistry (Anastas and Warner 1998), the processes to obtain fibers showed high yields (90% or more), consequently reducing the amount of byproducts. Obtaining fibers with such yields (90%) implied the use of more aggressive treatments. Thus, cold defibering (MP) presented a practically complete exploitation, taking in account the fiber barks. The chemical composition of MP can be considered almost equal to the orange tree pruning wood (Gonzalez *et al.* 2011). Fibers obtained by thermomechanical processes showed a lower yield due to the removal of extractives and some soluble hemicelluloses. In the case of chemi-thermomechanical pulp, in addition to removing hemicelluloses and extractives (Boras and Gatenholm 1999), the orange tree pruning wood was slightly delignified. The process yield was reduced to approximately 90%. The different processes modified the chemical composition of the fibers surfaces while increasing its bond capabilities. Consequently, as the yield decreased, the ability to create chemical bonds changed. The *TS* test outputs, increasing 141% from MP to TMP and 19% from TMP to CTMP, allowed for verification of this fact. In the papermaking field, *TS* is governed by three main parameters: the fibre strength, the fibre/fibre joint strength, and the number of efficient joints per volume (Marais and Wagberg 2012).

It is well known that the chemical composition of wood is mainly cellulose, hemicellulose, and lignin, and small amounts of other chemical components, such as resin and fatty acids, triglycerides, sterols, and steryl esters, usually classified as extractives (Johansson 2002). Despite different defibration and treatment techniques, the chemical percentage of carbohydrates and lignin of the whole pulps were approximately equal (Koljonen *et al.* 2003). However, differences were observed, both in the chemical

composition and morphology on the fiber surfaces (Boras and Gatenholm 1999; Koljonen *et al.* 2003). On the other hand, the surface composition could not be predicted from the bulk composition of the pulps (Boras and Gatenholm 1999; Johansson 2002; Koljonen *et al.* 2003). Results revealed that the surfaces of the fibers were covered by lignin and extractives. Figure 1, based on (Sundholm 1998) shows that the mean chemical bulk composition at the middle lamella level (middle lamella + primary wall) is essentially 19% cellulose and 23% hemicellulose, representing 42% of carbohydrates, and 58% lignin. These data are consistent with results of Koljonen *et al.* 2003, who found that 50 to 75% of the surface of the mechanical pulps (MP, TMP, and CTMP) was covered by lignin and extractives This is also consistent with the model of (Boras and Gatenholm 1999), with 50 to 55% of the surface covered by extractives and lignin and 49 to 45% by carbohydrates. The presence of lignin was also observed in the case of high temperature mechanical pulp (Bhattacharyya *et al.* 2003)

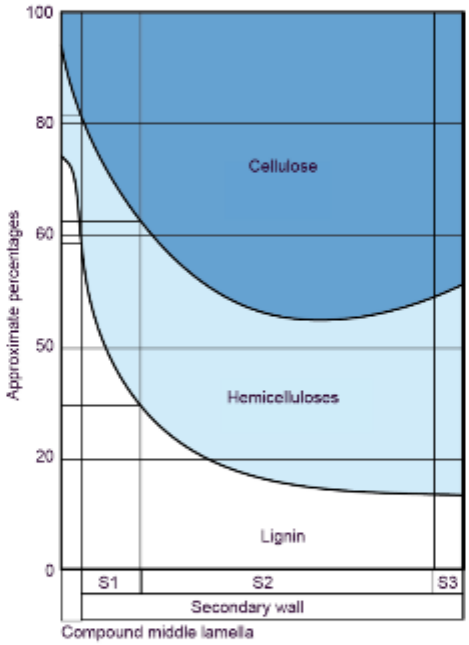

Fig. 1. Structure of wood fibers and chemical composition along its fibril structure. Figure created based on cited data in Sundholm (1998).

The changes in the chemical composition of the fibers surface, which led to the noticeable increase of the *TS*, can be explained as being a consequence of a higher accessibility to the chemical components able to generate hydrogen bonds or Van der Waals interaction. In that sense, it was expected that the MAPP also took advantage of the higher accessibility, improving the fiber-matrix interface.

Moreover, the evaluation of the cationic demand was performed by means of the colloid titration technique TTC (Carrasco *et al.* 1996; Rouger and Mutje 1984; Terayama, 1952). Table 2 shows the outcomes in microequivalents of polyDADMAC per gram of reinforcement. The gradual removal of the extractives by the treatments led to an increase of the hydrophilicity of the surfaces. In agreement with Lopez *et al.* (2012a), the cationic

demand decreased slightly with the insensitivity of the treatments. Probably the main contribution to surface charge density shown by the fibers is due to the presence of extractives in addition to lignin. In comparison to MP, TMP, and CTMP, the surface charge density displayed by bleached hardwood kraft pulps (19.20 μeq/g) is very low, probably due to the relative absence of extractives and lignin (Lopez *et al.* 2012a).

Taking into account that all the fibers were mechanically defibrated, it was observed that the weighted length of the fibers increased as the defibering benefited from the fibers treatments (cold water, steam, and NaOH 5% + steam). The changes in length were especially noticeable from MP to TMP, while they were minor from TMP to CTMP; this was probably due to the softening of lignin, a fact that facilitated the defibration (Flandez *et al.* 2012). Nonetheless, as a result of the loads during the composite preparation, the fibers experienced a reduction of their lengths, and the length distribution outside and inside the composite were not related (Karmaker and Youngquist 1996; Li *et al.* 2009; Vallejos *et al.* 2012).

As can be found in Table 1, the diameter of the fibers can be considered almost constant. Nevertheless, and as a consequence of the weighted length variation, the aspect ratio of the fibers increased with the intensity of the treatments form MP to TMP and remained similar from TMP to CTMP.

Interface, optimization of the composite tensile strength

Lignocellulosic fibers combined with hydrophobic thermoplastics as PP needed to be modified because effective wetting of the fibers and strong interfacial adhesion in order to achieve higher mechanical properties of the composite (Colom *et al.* 2003; de Carvalho *et al.* 2012; Osman *et al.* 2010). Different coupling agents exist, but in the research of PP reinforced with natural fibers (Li and Sain 2003), it is shown that the best results are obtained with the use of MAPP. The use of MAPP coupling agent promotes the interaction between OPF fibers and PP matrix at the interface due to the increase in the accessibility to OH groups. The proposed coupling mechanism is hydrogen bonding and also covalent ester linkage generated by the chemical reaction of the anhydride groups of the MAPP and the hydroxyl groups of the fiber surface (Mendez *et al.* 2007). In order to evaluate the micromechanics tensile properties of OPF, PP composite materials containing 0 to 8% MAPP content were prepared. In fact, the optimization of the MAPP percentage against composite strength, prevents the premature fiber slippage from the matrix by ensuring an enhanced anchorage of the fiber to the matrix and the exploitation of the reinforcing capabilities of the fiber (Lopez *et al.* 2011). In papermaking, and as demonstrated by Davison (1972), the weak link in paper dry strength is very often the fiber/fiber joint strength, and not the fiber itself. Additionally, the stoichiometry of the interaction between the fibers and the MAPP is discussed by Lopez *et al.* (2011).

Figure 2 shows the evolution of the tensile strength of the composites against the MAPP content. The tensile strength increased somehow linearly with the MAPP content, up to 6 wt% in the case of MP and TMP, and up to 4 wt% in the case of CTMP. It appeared that the accessibility of MAPP to OH groups and the ease for creation of hydrogen and ester bonds increased from MP to CTMP. The lower percentage of MAPP needed by CTMP composites to increase the tensile strength could be a consequence of the higher accessibility and extend of reaction.

It was found that for higher MAPP contents, the tensile strength tended to decrease. The decrease in tensile strength at the higher coupling agent contents is

attributed to self-entanglement among the coupling agent chains, rather than with the polymer, resulting in slippage (Beg and Pickering 2008). This result is in agreement with previous research, where it was found that, for different reinforcement fibers, although the optimum percentage of MAPP varied with the fiber content, a 6 wt% of MAPP delivered the best mean outputs (Lopez *et al.* 2011; Mendez *et al.* 2007; Vallejos *et al.* 2012).

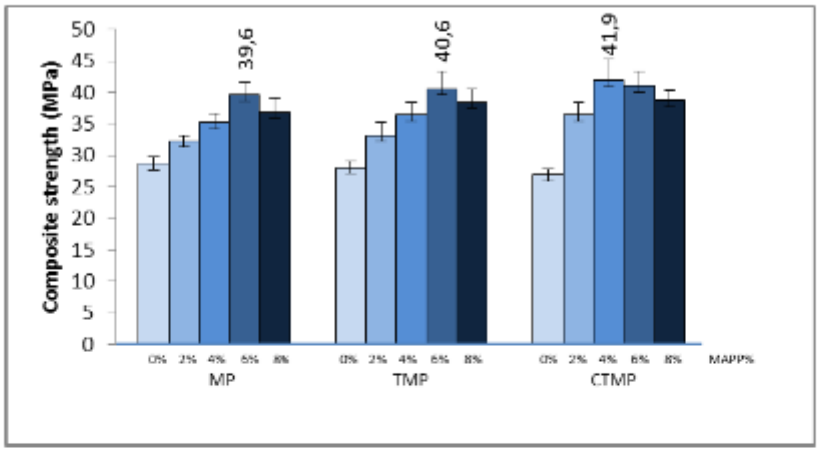

Fig. 2. Evolution of the 30 wt% CPF/PP composites strength against the MAPP content

Once the percentage of MAPP for the different PP/OPF composites was established, it was found that the obtained maximum σ_t^C were slightly different. In fact, the highest value of σ_t^C increased from MP to TMP by 2.5% and from TMP to CTMP by 3.2%, showing a high correlation with the behavior of the cationic demand that also changed slightly. If the results are compared with a 30% stone groundwood (SGW)/PP composite with 6% of MAPP (Lopez *et al.* 2011, 2012a), it is found that the SGW composites show 18% higher σ_t^C (46.7 MPa). The difference could be explained by the fact that SGW came from softwood and MP from hardwood. Usually the intrinsic strength of softwood fibers is higher than that of hardwood. On the other hand, the fibers surface chemical composition is also different, leading to a different extension of the reactions between the MAPP and the fibers surface.

Orientation factor, interfacial shear strength, and mean intrinsic tensile strength

Once the nature of the fibers was established and the understanding of the interface mechanism was improved, it was possible to initiate the evaluation of the micromechanics; in fact, this was the main objective of the present research. To solve the Kelly-Tyson equation by means of the Bowyer-Bader methodology, it was necessary to establish all the necessary input data (Eq. 1).

The Young's moduli of the composites were computed by the Hirsch model (Hirsch 1962) applied to the experimental values of the analyzed composites. Table 2 shows all of the input data needed to compute the moduli of the fibers. In all cases, the density of the matrix was 0.905 g/cm^3, and the factor β, that determines the transference of the stress between the fiber and the matrix, was 0.4 (Kalaprasad *et al.* 1997).

Table 2. Fiber and Composite Properties

	Weight (%)	ρ (g/cm^3)	V_f ($^o/_1$)	E_t^c (GPa)	E_t^m (GPa)	E_t^f (GPa)
MP (6% MAPP)	30	1.25	0.237	3.8	1.5	23.1
TMP (6% MAPP)	30	1.29	0.230	3.1	1.5	16.3
CTMP 4%(MAPP)	30	1.365	0.220	2.94	1.5	15.3

Composite compounding and processing entails a reduction of the fibers lengths (Li *et al.* 2009; Vallejos *et al.* 2012). The shortage is probably attributable to the attrition that happens during the compounding and processing of the composites (Bourmaud and Baley 2007; Karmaker and Youngquist 1996). Hence it was necessary to obtain the length distributions of the fibers inside the composites (Fig. 3). In fact, the values of the mean weighted lengths inside the composite were 256, 310, and 331 µm for the MP, TMP, and CTMP, respectively. The corresponding percentages of shortening were 22%, 36%, and 32%, respectively.

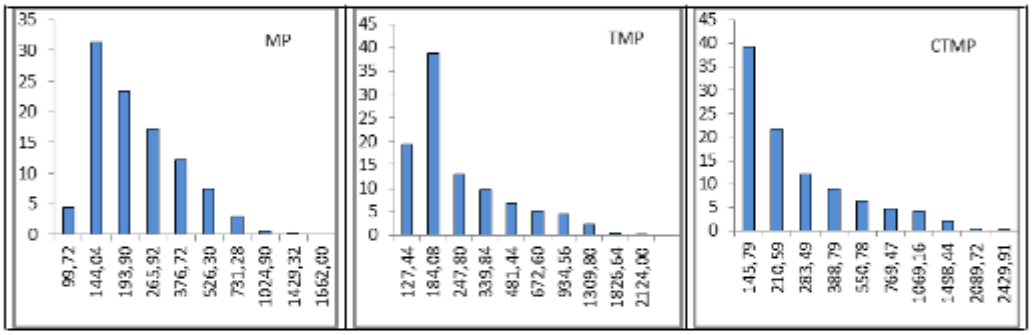

Fig. 3. Fiber length distributions inside the composite material. Length percentage against fiber weighted length

From the experimental results, and once the fiber distributions were known, it was possible to apply the Bowyer-Bader methodology. Table 3, in which ε_t^c is the strain at composite failure, summarizes the mean experimental data outputs. The values of the properties for the two strain levels (a quarter and a half from breaking point), needed to apply Bowyer-Bader methodology, were obtained from the experimental outputs.

Table 3. Experimental Composite Mechanical Properties at Breaking Point and at One-Quarter and One-Half of the Breaking Point

	ε_t^c (%)	σ_t^c (MPa)	σ_t^{m*} (MPa)	$\varepsilon_t^{c\ (1/4)}$ (%)	$\sigma_t^{m*\ (1/4)}$ (MPa)	$\sigma_t^{c\ (1/4)}$ (MPa)	$\varepsilon_t^{c\ (1/2)}$ (%)	$\sigma_t^{c\ (1/2)}$ (MPa)	$\sigma_t^{m*\ (1/2)}$ (MPa)
MP	4	39.6	25.7	1.00	12.0	22.6	2.00	33.9	19.2
TMP	4.3	40.6	26.3	1.08	13.2	19.8	2.15	31.2	20.0
CTMP	4.6	41.9	27.0	1.15	14.2	20.6	2.30	31.9	20.5

Once the Bowyer-Bader methodology was applied, the values for τ, χ_1, and l_c were obtained, as shown in Table 4. Taking into account that $\chi_1 = \cos^4\theta$, the obtained

orientation factors (χ_1) for the different OPF, implied mean orientation angles of 40.5°, 43.1°, and 42.9° for the MP, TMP, and CTMP, respectively. The found angles were similar and showed that fiber treatments slightly affected the orientation angle.

The critical fiber length (l_c^f) was calculated from $l_c^f = (d^f \sigma_t^C)/2\tau$ (Li *et al.* 2009).

The obtained values of the interfacial shear strength (τ), considering the σ_t^m of the PP (28.4 MPa), were within or close to the range derived from the application of Von Misses and Tresca criteria (16.4 MPa and 14.2 MPa, respectively (Pegoretti *et al.* 1996; Vilaseca *et al.* 2010). The interfacial shear strength increased slightly with the intensity of the OPF treatments.

Once the values for χ_1 and τ were obtained, the Kelly-Tyson modified equation was used (Kelly and Tyson 1965; Lopez *et al.* 2011; Vallejos *et al.* 2012) to obtain a value for σ_t^F for all the tested composites (Table 4). The obtained values of σ_t^F for MP, TMP, and CTMP composites increased with the intensity of the treatments, noticeably from MP to TMP and slightly from TMP to CTMP.

Table 4. Micromechanics Properties of the Formulated Composites

	τ (MPa)	χ_1	l_c (μm)	σ_t^f (MPa)
MP	16.00	0.335	303	512
TMP	16.03	0.284	309	547
CTMP	16.74	0.288	307	549

The values of the orientation factor were around 0.3, which is very similar to the corresponding value for SGW (Lopez *et al.* 2011). The critical length of the fibers was similar. The interfacial shear strength increased slightly from MP to CTMP and had a value around 16 MPa, which is very similar to that of SGW (15.71 MPA). At the same time, the intrinsic tensile strength increased with the intensity of the treatments, and as expected, due to the above-mentioned differences between fibers from hardwood and softwood, was 20% smaller than the mechanical pulp from SGW's mean intrinsic tensile strength (612 Mpa) (Lopez *et al.* 2011).

Equation 1 can be simplified to $\sigma_t^C = \chi_1(X+Y)+Z$ where X, Y, and Z are the contribution of the subcritical fibers, supercritical fibers, and the matrix to the composite strength (σ_t^C). Values for X, Y, and Z were deduced from Eq. 2. To estimate the final contribution to the composite, X and Y must be multiplied by χ_1.

As it can be observed in Table 5, the contribution of the matrix remained almost constant, with a value around the 50% of the total for all the materials. It was also observed that the contributions of the subcritical fibers were the less relevant. The contribution of the subcritical fibers decreased from 18.5% to 11.1% from the MP to the TMP. Its value was similar for the case of TMP and CTMP.

Table 5. Nominal and Percentage Contribution of the Subcritical (*X*) and Supercritical (*Y*) Fibers, and the Matrix (*Z*) to the Strength of the Composite Materials

	$X \cdot \chi_1$ (MPa, %)	$Y \cdot \chi_1$ (MPa, %)	Z (MPa, %)
MP	7.35 18.5%	12.64 32.0%	19.61 49.5%
TMP	4.51 11.1%	15.87 39.1%	20.22 49.8%
CTMP	4.75 11.3%	16.13 38.6%	21.02 50.1%

It was observed that the contribution of the matrix remained almost constant and equivalent to the 50% of the final composite strength. The contribution of the subcritical fibers decreased noticeably from MP to TMP and remained almost constant from TMP to CTMP. Consequently, the relative contribution of the supercritical fibers increased.

CONCLUSIONS

In this work, the micromechanical parameters of mechanical, thermomechanical, and chemi-thermomechanical pulps from orange tree pruning, as reinforcement of a polypropylene matrix, were characterized. From the results it was found that:

1. The treatments used to obtain mechanical pulp (MP), thermomechanical pulp (TMP), and chemi-thermomechanical pulp (CTMP) from orange tree pruning fibers (OPF) caused changes in the chemical composition of the fiber surfaces. The changes were made evident by the tensile strength of the paper (papermaking route), but not so much by the extent of the compatabilizer/fiber surface reaction. The research allowed a better understanding of the bonding mechanism in the interface between matrix and reinforcing fibers.
2. The tensile strength increased from MP to CTMP composites, but the process yield decreased. The slight increments of the tensile strength hardly justify the use of CTMP processes with OPF.
3. The mean orientation factor for the injection-molded composite materials was about 0.3 with a 42.3° mean orientation angle, configuring a short fiber semi-aligned composite
4. The interfacial shear strength values stand within or close to the interval derived from the application of the Von Misses and Tresca criteria, and are similar to those of mechanical pulp from softwood (SGW).
5. The intrinsic tensile properties of the fiber for the coupling agent-enhanced composite materials are similar for MP, TMP, and CTMP and inferior to that of SGW.
6. The use of MP from OPF is shown as a source to add value to agroforestry waste, extending the value chain for the agricultural industry, providing low cost alternatives to wood fibers, and reducing the need for burning.

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4 TENSILE PROPERTIES OF POLYPROPYLENE COMPOSITES REINFORCED WITH MECHANICAL, THERMOMECHANICAL, AND CHEMI-THERMOMECHANICAL PULPS FROM ORANGE PRUNING

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Tensile Properties of Polypropylene Composites Reinforced with Mechanical, Thermomechanical, and Chemi-Thermomechanical Pulps from Orange Pruning

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This paper explores the evolution in the tensile strength of orange pruning fiber-reinforced polypropylene composites. The exploitation of these pruning's can effectively avoid incineration, with the consequence of CO_2 emissions and fire risk, while extending the value chain of the agricultural industry. This biomass was subjected to three different treatments yielding mechanical, thermomechanical, and chemi-thermomechanical pulps. It was found that 20 to 50% of these pulps, together with a coupling agent, were used as polypropylene reinforcement. The evolution in the tensile strength and morphological properties of the fibers, and the effect of treatments on these properties were analyzed. A modified rule of mixtures (mROM) was used to analyze the micromechanical properties of the interface. In addition, the mechanical properties were weighted against the fiber treatment yields. Finally, factors to compute the net contribution of the fibers to the final strength of the composite materials were proposed.

Keywords: Composite materials; Tensile properties; Green composites; Pruning recovery

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INTRODUCTION

During recent years, there has been increased environmental awareness of the use of composite materials through scientific literature (Mohanty *et al.* 2002; Yu *et al.* 2006). In effect, a great amount of research has been devoted to the substitution of glass fibers (GF) by natural fibers (Beckermann and Pickering, 2009; Ardanuy *et al.* 2012; Ho *et al.* 2012; Vallejos *et al.* 2012). Nonetheless, there are some authors who doubt the possibilities of natural fiber-reinforced composites as a viable replacement for GF-reinforced composites (Joshi *et al.* 2004). Anyhow, the scientific community has continued devoting time to natural fiber-reinforced composites. The main concern about GF-reinforced composites has been the difficulties in designing a correct method for recycling and re-use of those materials, being that incineration for energy recovery is the most practical method (Corbière-Nicollier *et al.* 2001). While incinerating the composites produces energy recovery, it only results in a portion of the energy needed to produce the GF and the matrix. However, using GF results in wear of the preparation and manufacturing equipment (Ali *et al.* 2011; Nedjma *et al.* 2013). On the other hand, the use of natural fibers as reinforcements ensures the conservation of more environmental friendly materials, referred to as green composites. Using the twelve principles of green chemistry (Anastas and

Warner 1998) as a reference, the substitution of GF by natural fibers is in agreement with some of these principles. Natural fibers clearly represent a "use of renewable feedstocks," and compared with GF, natural fibers are safer materials.

There are many possible sources for natural fibers, which include annual plants, wood, secondary fibers, and agroforestry or industrial wastes. Therefore, it seems interesting to use waste by-products as the source in reinforcing fibers for value. Moreover, exploitation into the pruning methods will prevent their incineration and the consequent carbon dioxide (CO_2) emissions. Consequently, the use of waste from agriculture seems favorable. Specifically, the use of citrus pruning ensures an annually renewable source of materials, as the amount produced in Spain represents 1.15×10^9 kg/year (Reixach *et al.* 2013b). Additionally, and from a strategic point of view, extending the value chain of the agroforestry industries by the valorization of co- and by-products would enhance the profitability of these industries (Mishra and Sain 2009). In the case of the Mediterranean arch countries, citrus pruning represents a stable, renewable, and readily available source of wood fibers.

Wood fiber-reinforced composites have been widely studied and characterized (Saheb and Jog 1999; Xu *et al.* 2008; Sobczak *et al.* 2013; Schirp *et al.* 2014). Many works have been published concerning the tensile properties of such materials (Beg and Pickering 2008; Vilaseca *et al.* 2008; Lopez *et al.* 2011, 2012; Monteiro *et al.* 2011; Fuqua *et al.* 2013). In previous research, tensile strengths between 28.6 and 56.2 MPa have been obtained, depending on the amount of reinforcement and the addition or not of coupling agents (Lopez *et al.* 2011). It was discovered that the lower values were attributable to an unfavorable interphase between the fibers and the matrix. Wood fibers are hydrophilic, while polypropylene (PP) is hydrophobic. Therefore, fiber treatments or the use of coupling agents prevent a bad interphase. Some works propose the use of maleated polypropylene (MAPP) as a solution to this problem. In fact, adding a low (4 to 6%) concentration of MAPP enhanced the tensile properties (Lopez *et al.* 2011; Lopez *et al.* 2012). In summary, wood fibers are a comparatively superior source of composite reinforcement. Focusing on the use of tree pruning as reinforcement has not been widely presented in the literature. There are some studies on obtaining composite materials from tree pruning (Hermawan *et al.* 2009; Cruz-Estrada *et al.* 2010; Sahin and Arslan 2013; Yeniocak *et al.* 2014); however these articles are mainly devoted to the chemical properties of the fibers or the manufacturing of the boards. When the authors decided to study the use of orange tree pruning fibers (OPF) as PP reinforcement, they found only a few related studies. Actually, some of the authors have published works on the optimization of the interface of the OPF-PP composites and the micromechanic properties (Reixach *et al.* 2013b), and on the Young's modulus of such composites (Reixach *et al.* 2013a). Also, in a recent article, the chemical composition of the orange tree pruning was studied (Gonzalez *et al.* 2013).

Wood fibers from citrus pruning could be directly used as polypropylene reinforcement, with an almost 100% yield with respect to the raw material (Reixach *et al.* 2013b). There has been some research on the integral use of wood fibers, with good results; however, the presence of lignin and extractives in the fiber's surface could diminish the contribution of the reinforcement fibers to the final tensile properties of the composites, blocking the creation of hydrogen bonds (Lopez *et al.* 2012). Therefore, with the objective of obtaining better fiber matrix interphases, some authors proposed the chemical treatment of the fiber's surface, with the objective of removing part of the lignin and the extractives. Depending on how drastic the treatments are determines the decrease on the yield of the reinforcing fibers against the raw material. Usually, the fibers obtained are called, in

decreasing yield order: mechanical pulp (MP), thermomechanical pulp (TMP), and chemi-thermomechanical pulp (C-TMP). The treated fibers usually show different chemical and morphological properties. The yields of such treatments are between 90 to 100%, and the amount of by-products produced is comparatively low. To the best knowledge of the authors, there are no studies on the weighted net contribution yields of the reinforcement fibers. Therefore, it seemed necessary to investigate the increases of the tensile properties against the decreasing yields to establish the relative net contribution of the raw materials to the composites.

In this study, the macro- and micro-mechanical tensile properties of the MP, TMP and CTMP from OPF reinforced PP composites are investigated. The neat contribution of the fibers to the final strength of the composites was computed by using a fiber tensile strength factor. Finally, the tensile properties were outweighed against the treatment yields, to stablish the net contributions of the reinforcement fibers in relation to the used raw material.

EXPERIMENTAL

Materials

The composites were prepared using polypropylene (PP) (Isplen PP099 K2M) by Repsol-YPF from Tarragona, Spain, which was characterized by its low crystallinity and density of 905 kg/m^3. Maleated polypropylene (MAPP), Epolene G3015 with acid number 15 mg KOH/g by Eastman Chemical Products (San Roque, Spain) was used as the coupling agent. As reinforcement, biomass from orange tree pruning fibers (OPF) were used and kindly supplied by Mas Clarà de Domeny, Girona, Spain. Chemical reagents, sodium hydroxide and anthraquinone, were supplied by Merck KGaA (Darmstadt, Germany) and BAYER AG (Germany), respectively. The rest of the reagents used in this work were diethyleneglycol dimethyl ether (diglyme) provided by Clariant (Barcelona, Spain), decahydronaphthalene (decalin) provided by Fischer Scientific (Madrid, Spain).

Methods

Preparation of orange tree pruning derivatives

The OPF's were obtained following the methodology described by Reixach *et al.* (2013b). Prior to any specific treatment, all OPF was crushed and classified with a knives mill. MP was obtained by defibering in a Sprout-Waldron mill. To obtain TMP, the classified OPF were heated to 160 ºC during 30 min and then defibered. The CTMP was obtained by a 5% NaOH, 0.1% anthraquinone cooking at 160 ºC for 20 min in a liquid to fiber 1:4 ratio. Then the slurry was washed and defibered.

Compounding

Composite materials comprising 20 to 50 weight percent (wt-%) PP-OPF were obtained. The MP and TMP-reinforced composites added 6 wt-% to MAPP, and the CTMP at 4 wt-%. All the composites were added at the amount of coupling agent suggested in previous work (Reixach *et al.* 2013b). In the cited work the tensile strength of the composites was tested against the amount of MAPP. It was found that the proposed percentages of MAPP rendered the best tensile strengths. Before the preparation of the composites the materials were processed in a Gelimat multi-kinetic mixer (Dusatec, Inc., Ramsey, NJ, USA). The mixing was carried out at 2500 rpm for 2 min until a 210 ºC

temperature was obtained. The fibers were submitted to lesser attrition loads in a multi-kinetic mixer than in a Brabender mixer, being the result composites with fibers with higher aspect ratios and consequently better tensile properties (Lopez *et al.* 2012). The resulting blends were ground with mill knives, dried, and stored at 80 °C for at least 24 h before processing.

Composite processing and mechanical characterization

The composites were injection molded, at 190 °C, to produce dog bone test specimens. The specimens were produced in a steel mould and using a Meteor 40 (Mateu & Sole, Spain) injection machine. After a 48 h conditioning time at 23 °C and 50% relative humidity, the specimens were subjected to tensile testing in a 1122 Instron universal machine, in order to determine their tensile strength and ultimate strain. The Composite mechanical characterization was carried out according to ASTM D638.

Fiber extraction from composites and morphological analysis

Reinforcing fibers were extracted from the matrix by decalin-based solubilization of the matrix in a Soxhlet apparatus,

A morphological analysis of the fiber length and diameter was performed using a MorFi Compact (Morphological fiber analyzer, Techpap SAS, France). A map of the fiber's diameter and length distribution was obtained from two samples.

Fiber tensile strength factor (FTSF)

A modified rule of mixtures (mROM) for the tensile strength (Thomason, 2002) is a good micromechanical model as long as the behavior of the strength is linear against the fiber volume fraction. The mROM is defined by the following equation,

$$\sigma_t^C = f_c \cdot \sigma_t^f \cdot V^f + (1 - V^f) \cdot \sigma_t^{m*} \quad (1)$$

where, σ^C is the tensile strength of the composite (MPa), σ^f the intrinsic tensile strength of the fibers (MPa), and σ^{m*} is the matrix tensile stress at the failure point of the composite (MPa). V^f is the volume fraction of the reinforcement. Since the fibers were not aligned, the compatibility factor (f_c) accounts for the orientation effect on the contribution of the fibers. While there are methods to measure σ^f, the size of the fiber makes this difficult or impossible to predict. The authors proposed, in a previous work, a fiber tensile strength factor (*FTSF*) (Lopez *et al.* 2012), by rearranging the mROM (Eq. 2),

$$\sigma_t^c - (1 - V^f)\sigma_t^{m*} = f_c \cdot \sigma_t^f V^f = FTSF \quad (2)$$

where the terms, $f_c \cdot \sigma_t^f$ amount for the contribution of the fibers to the composite tensile strength, equaling the slope of a line, and is the function of the fiber volume fraction.

RESULTS AND DISCUSSION

Tensile Strength of the Composites

Certain factors are generally known to influence the final tensile strength of a composite. The most widely known and referenced are the chemical and physic properties of the matrix and the fibers, the dispersion of the fibers inside the composite, the aspect

ratio of the reinforcement fibers (ratio between the fiber mean length and diameter), the relative orientation of the fibers to the load, and the ability of the fiber matrix interphase to withstand the shear load matrix (Thomason, 2002; Vilaseca *et al.* 2010; Lopez *et al.* 2011; Vallejos *et al.* 2012; Serrano *et al.* 2013). Out of all the properties, the most influential is the quality of the interphase. Prior work by some of the authors established that adding 6 wt-% of MAPP to the MP and TMP-reinforced composites, and a 4 wt-% of MP and TMP to the CTMP, ensured favorable tensile properties (Reixach *et al.* 2013b). Results in Table 1 shows the stress-strain tests and the morphological analysis of the fibers extracted from the composites.

Table 1. Tensile Properties and Morphological Properties of Composite Fibers with Varying OPF Content

		OPF Content			
		20%	30%	40%	50%
MP	V_f	0.153	0.237	0.326	0.420
	σ_t^c (MPa)	34.9 (0.76)	39.6 (0.68)	44.5 (0.92)	50.1 (1.51)
	ε_t^c (%)	5.2 (0.23)	4.0 (0.16)	2.8 (0.15)	2.16 (0.12)
	l_f (µm)	268	256	241	234
	d_f (µm)	20.1	19.8	19.6	19.7
	l_f/d_f	13.3	12.9	12.3	11.9
TMP	V_f	0.149	0.231	0.319	0.412
	σ_t^c (MPa)	36.3 (0.63)	40.6 (0.71)	45.9 (0.79)	52.3 (0.96)
	ε_t^c (%)	5.5 (0.17)	4.3 (0.13)	3.0 (0.14)	2.61 (0.08)
	l_f (µm)	327	310	290	282
	d_f (µm)	19.3	19.4	19.5	19.3
	l_f/d_f	16.9	15.9	14.9	14.6
CTMP	V_f	0.142	0.221	0.307	0.399
	σ_t^c (MPa)	37.2 (0.78)	41.9 (0.64)	46.5 (0.84)	53.1 (1.16)
	ε_t^c (%)	5.9 (0.14)	4.6 (0.21)	3.8 (0.18)	3.1 (0.15)
	l_f (µm)	350	331	311	301
	d_f (µm)	19.4	19.6	19.7	19.7
	l_f/d_f	18.4	16.8	15.8	15.3

V_f : reinforcing fiber volume fraction. σ_t^c : tensile strength of the composite(MPa). ε_t^c : strain at break of the composites (%). l_f : mean fiber length (µm). d_f: mean fiber diameter (µm). l_f/d_f : aspect ratio. The standard deviations are inside the parenthesis.

Figure 1 shows how the tensile strength of all the composites tended to increase linearly with increasing fiber content. At 50% MP, TMP, and CTMP content for OPF-reinforced composites, tensile strengths were 76%, 84%, and 87% improved over the matrix property (28.4 MPa at 8.87% elongation). In general, the CTMP fibers showed a 1.5% higher reinforcement capacity compared to the TMP fibers, and 5.9% above that of the MP fibers. It was also found that the standard deviations of the tensile properties remain similar from one kind of reinforcement to the other.

While the TMP and CTMP fibers exhibited similar properties, the MP-reinforced materials showed slightly lower values. This may have occurred because of the intrinsic properties of the fibers, or the number of bonds per volume unit, or the quality of the fibers, represented by the interphase shear strength (τ) between the reinforcement and the matrix (Carrasco *et al.* 1996; Vallejos *et al.* 2012). In a recent article the authors discussed the micromechanic tensile properties of 30% reinforced OPF-PP composites (Reixach *et al.* 2013b). They found that the MP, TMP, and CTMP-reinforced composites were 16.00 MPa, 16.03 MPa, and 16.74 MPa, respectively. The results indicated that the interphase strength

was minimally influenced by the fiber treatments. The same work showed that the orientation factor (χ_1) of the fibers inside the composite, for the same reinforcements, were 0.335 MPa, 0.284 MPa, and 0.288 MPa, respectively. The values could be translated to orientation angles using the relation: $\chi_1 = cos^4(\phi)$ (Vallejos *et al.* 2012). The computed angles were 40.5°, 43.1°, and 42.9°, respectively. Since the angles were similar, it may indicate that the treatments minimally affected the orientation of the fibers inside the composite, after controlling for the effect of the equipment and the geometry of the mould (Vallejos *et al.* 2012). Similarly, it was found that the intrinsic tensile strengths of the MP, TMP, and CTMP OPF-reinforced fibers (σ_f^*) were 512 MPa, 547 MPa, and 549 MPa, respectively. The differences found in the σ_f^*s could explain the increase in the tensile strengths of the TMP and CTMP-reinforced composites, compared to that of the MP-reinforced composites.

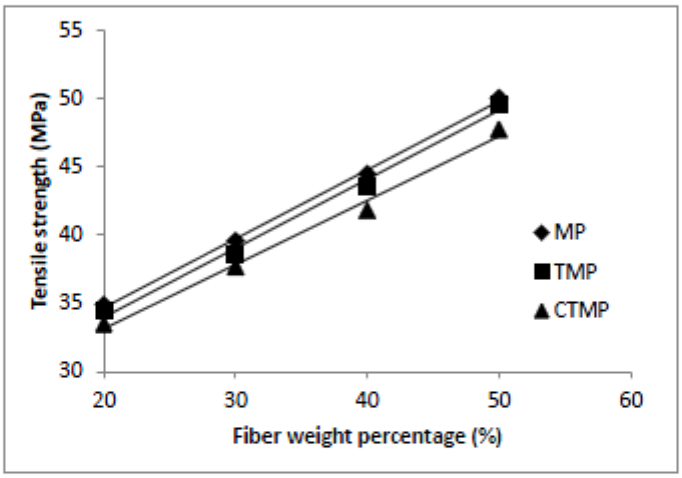

Fig. 1. Tensile strength of the MP, TMP, and CTMP-PP-reinforced composites

In parallel, the morphological analysis results (Table 1) showed that the mean fiber length decreased as the percentage of reinforcement increased, independent of the treatment. This decrease may have occurred because of the attrition during the composite preparation and specimen mould injection (Karmaker and Youngquist 1996; Bourmaud and Baley 2007). Usually the attrition is amplified by the presence of coupling agents, because there are more bonds available between the reinforcement and the matrix (Lopez *et al.* 2011; Vallejos *et al.* 2012). It was also verified that the CTMP fibers were slightly longer than the TMP and the MP fibers. On the other hand, the diameters of the fibers were minimally affected during the treatments, and therefore were considered constant. The consequences of longer lengths and the similar diameters per treatment were that the aspect ratios for the CTMP fibers increased, which could be used to explain the better tensile properties observed in the CTMP-reinforced composites.

While the dispersion of the fibers inside the matrix highly affected the properties of the composites, a recent article found that the MP, TMP, and CTMP-reinforced composites exhibited favorable dispersion rates (Reixach *et al.* 2013a). Based on the results from this article, it contradicts the lack of dispersion as the cause of the improvements in the tensile strengths.

Apparently, CTMP-reinforced PP composites yielded the most competitive materials. However, if the properties were weighted against the treatment yields (η_p) (1, 0.95, and 0.9), with respect to the raw fibers (MP, TMP, and CTMP), the conclusions were changed. The weighted tensile strengths (σ_{tw}^C) were calculated by: $\sigma_{tw}^C = \sigma_t^C / \eta_p$. Figure 2 shows the weighted properties for the MP, TMP, and CTMP fibers, and it was found that the MP and TMP fibers' tensile strengths were greater than those of the CTMP fibers.

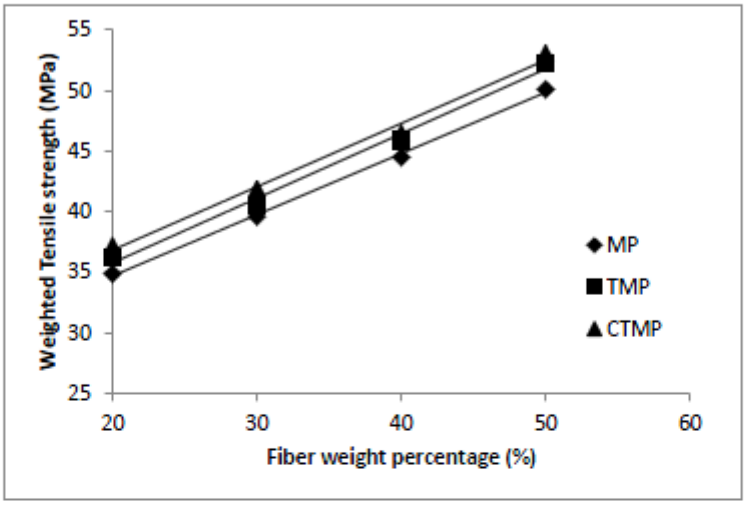

Fig. 2. Weighted tensile strengths for MP, TMP, and CTMP-PP-reinforced composites

Regarding other reinforcements, the obtained tensile strength values for the MP fibers were inferior to that of the stone ground-wood (SGW) MP-reinforced PP composites, which exhibited tensile strengths between 40.6 and 56.2 MPa for 20 to 50 wt.% fiber contents (Lopez *et al.* 2012). Generally speaking, OPF MP-reinforced composites showed similar tensile strengths to the SGW MP-reinforced composites, with less than 10% fiber content. Similarly, the OPF CTMP-reinforced composites exhibited lower values than the SGW CTMP composites, with tensile strengths between 44.9 and 68.1 MPa. It seemed that the differences in the tensile strengths were not because of the interphase; OPF and SGW showed similar interphase shear strengths of 16.00 MPa and 15.58 MPa, respectively. The cause could be attributed to the intrinsic tensile strengths of the fibers, with values between 512 and 549 MPa for the OPF and 600 to 640 MPa for the SGW. The differences could be related to the physic-chemical properties of the fibers or the integral use of the pruning, especially in the case of the SGW where the barks were discarded (Lopez *et al.* 2011).

Compared with old newspaper recycled fibers (ONPF)-reinforced PP composites, with tensile strengths between 34.6 and 49.6 MPa, for 20 to 50% wt.% fiber contents (Serrano *et al.* 2014), OPF composites obtained similar or better results. When compared with glass fiber (GF)-reinforced PP composites, the 50% OPF composites showed tensile strengths similar to those obtained with a 20% GF-reinforced composites (Lopez *et al.* 2012). If a 6 wt-% of coupling agent was added to the GF composites, then the 50% OPF composites showed tensile strengths equivalent to a 12 wt-% GF-reinforced composite (Lopez *et al.* 2012).

To further study the behavior of tensile strengths, it was decided to extend the study to the contribution of the fibers.

Contribution of the Fibers to the Tensile Strength of the Composites

Attending to the linear behavior of the tensile strengths, the defined mROM (Eq. 1) could be considered as a micromechanical model to predict some micromechanical tensile properties of the composite. Therefore, the experimental data (Table 1) were used to compute the FTSF that corresponds with the slope of the line presented in the Fig. 3.

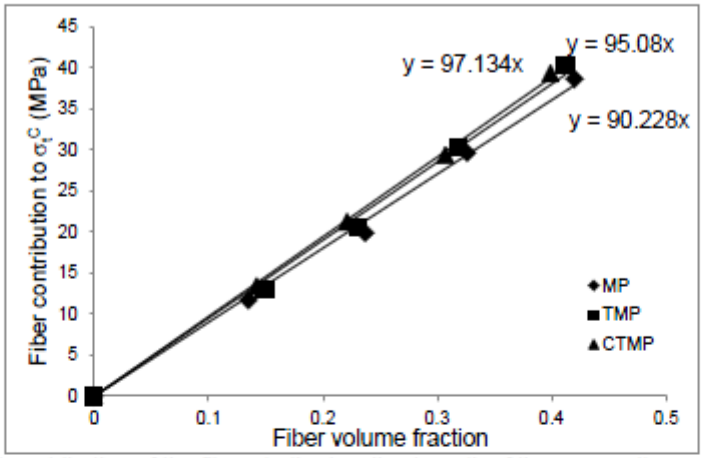

Fig. 3. The net contribution of the fibers to the tensile strength of the composites against fiber volume fractions

As shown in Fig. 3, the highest net fiber contribution was obtained from the CTMP fibers, with a slight advantage over the TMP and MP fibers. The computed FTSFs were inferior to that obtained for the SGW, which were 109.35 to 132.35 MPa. Similarly, the ONP fibers obtained values between 111.24 and 99.61 MPa (Serrano *et al.* 2014), that were additionally superior to that of OPF. Finally, compared with a GF FTFS estimate equaling 249.51 MPa, the net contribution of the OPF was clearly inferior. These lower values were mainly because of the comparatively (f_c = 0.2 for SGW) lower values for the intrinsic tensile strengths that were 46% higher in the case of SGW.

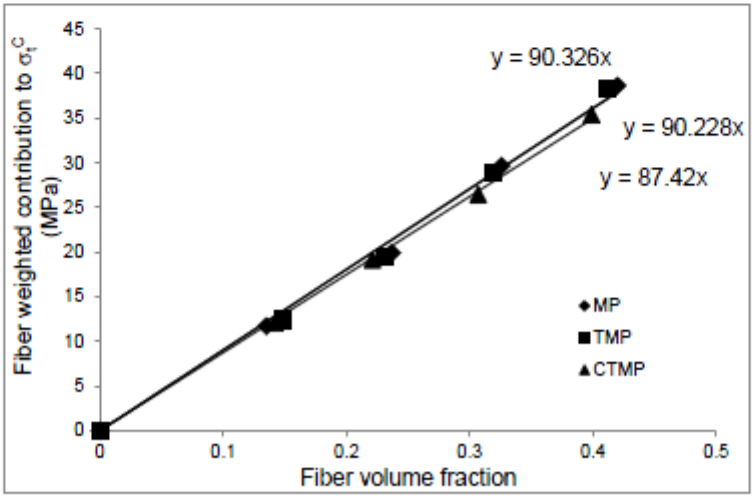

Fig. 4. The net weighted contribution of the fibers for the tensile strength of the composites against fiber volume fractions

If the FTSF was computed from the weighted tensile strengths (Fig. 4), the highest net fiber contribution corresponded to the TMP; however, it was virtually the same as the MP, and slightly higher than the CTMP fibers.

Tensile Strength Micromechanics

Table 2 shows the values of the coupling factors (f_c) for the different fiber treatments and fiber contents. It was accepted that a 0.2 coupling factor reveals optimum interphases for semi-aligned short fiber composites (Lopez *et al.* 2011). The coupling factors of the TMP and CTMP fibers only slightly increased with increasing fiber content. In the case of MP-reinforced composites, the coupling factor increased linearly with the increasing fiber content. All the 50% OPF-reinforced PP composites had coupling factors equal to or near 0.18, which supported the hypothesis that interphase had an insignificant role in the tensile strength improvements from one treatment to other.

Table 2. Matrix Contributions to Tensile Strengths, Coupling Factors, Length Factors, and Interphase Factors

		OPF Content			
		20%	30%	40%	50%
MP	V_f	0.153	0.237	0.326	0.420
	σ_f^{m*} (MPa)	26.8	25.8	22.0	19.7
	f_c	0.15	0.16	0.17	0.18
	χ_2	0.45	0.48	0.51	0.54
TMP	V_f	0.149	0.231	0.319	0.412
	σ_f^{m*} (MPa)	27.3	26.0	22.7	20.5
	f_c	0.17	0.17	0.18	0.18
	χ_2	0.60	0.60	0.63	0.63
CTMP	V_f	0.149	0.231	0.319	0.412
	σ_f^{m*} (MPa)	27.7	26.5	24.7	22.9
	f_c	0.16	0.16	0.16	0.17
	χ_2	0.55	0.55	0.55	0.60

V_f: reinforcing fiber volume fraction. σ_f^{m*}: matrix tensile stress at the failure point of the composite (MPa). f_c: Compatibility factor. χ_2: fiber length and interphase factor.

The f_c can be presented as the multiplication between the fiber length and interphase factor (χ_2), and the orientation factor(χ_1) (Sanadi *et al.* 1994). It has been found that the length and interphase factors were higher for the CTMP and TMP fibers, than the MP fibers. This can be attributed to a higher influence of such factors and the effect of the aspect ratio on the composite tensile strengths.

CONCLUSIONS

1. Fibers from orange tree pruning were competitive as a polypropylene reinforcement, exhibiting tensile strengths equivalent to that of a 20% glass fiber-reinforced polypropylene composite, when used at a 50 wt-% level.
2. The dispersion of the fibers inside the composite, the interphase quality, and the orientation angle of the fibers showed minimal variation against treatment of the fibers. On the other hand, there were changes in the aspect ratios and the intrinsic tensile

strengths of the fibers against treatment, with higher values observed in the CTMP and TMP-reinforced composites than the MP-reinforced composites.

3. If the tensile strength was weighted against the treatments yields, the most competitive materials were those reinforced with MP fibers. Usually, a process yield has a direct impact on the final cost of a product. The weighted property accounts for that cost. More importantly, by eliminating intermediate processing, products, and wastes, the principles of green chemistry are observed.
4. The fiber tensile strength factor (FTSR) was a valuable way to compare the net contribution of the fibers to the composite tensile strength. The FTSR was especially useful when the intrinsic strength of the fibers was unknown or difficult to measure.

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5 MODELING OF THE TENSILE MODULI OF MECHANICAL, THERMOMECHANICAL, AND CHEMI-THERMOMECHANICAL PULPS FROM ORANGE TREE PRUNING

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Modeling of the Tensile Moduli of Mechanical, Thermomechanical, and Chemi-Thermomechanical Pulps from Orange Tree Pruning

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Stiffness is one of the most relevant properties of composite materials. Although fiberglass has been traditionally used as reinforcement, natural fibers are seen as possible replacements due to concerns for environmental protection. In this work fibers from orange tree prunings were prepared and converted into mechanical, thermomechanical and chemi-thermomechanical pulps, to be used as reinforcement for polypropylene. Polypropylene composite materials with 20–50% of reinforcing fibers were prepared and mechanically characterized. The intrinsic Young's modulus of the fibers was back calculated by means of the Hirsch model. The moduli were also obtained by Halpin-Tsai equations with Tsai-Pagano methods and then compared to establish the influence of the aspect ratio. Finally, a fiber tensile modulus factor was defined in order to characterize the contribution of the fibers to the Young's moduli of the composites. POLYM. COMPOS., 34:1840–1846, 2013.

INTRODUCTION

Natural fibers from agroforestry are an attractive source of reinforcement for thermoplastic polymers. The reasons being their environmental friendliness, as opposed to synthetic fibers, and some other advantages thanks to their flexibility and which allow good aspect ratios after harsh composite fabrication methods to be maintained [1]. Although, glass fibers (GF) are the most commonly used reinforcement for structural purposes, natural fibers can be preferable in applications where, due to its specific properties, stiffness and weight are primary concerns [2,3]. Nonetheless, there are some authors that claim that when held up against GFs, natural fibers fail the same high performance requirements, and their use for structural purposes is currently impossible [2]. However, the reality is that natural fiber reinforced composites (FRP) are used in the automotive and building industries [4] for instance, in door panels, car roofs, and so forth. Other areas where the use of natural FRP would be opportune are in the packaging and furniture industries [5,6].

For structural and semistructural applications, the most relevant properties are probably stiffness and dimensional stability [4]. Natural fibers, due to their good specific properties, could achieve their own niche of competitiveness in semistructural applications, and with more research to improve their mechanical properties, moisture resistance, and durability, natural FRP could potentially become commonly used for structural purposes [2]. Lopez et al. [3,7] found a 1.07 ratio between the Young modulus of a 30% GF-polypropylene(PP) and 50% mechanical pulp (MP) from stone groundwood (SGW)–PP composites.

To predict the elastic properties of the composite materials, the elastic properties of the fibers need to be known

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and are defined as the average slope in the stress-strain curve in the strain interval from 0 to 0.3% [4]. Unfortunately, and due to their characteristics, the experimental evaluation of the Young's modulus of natural fibers is costly and difficult, and sometimes even impossible. The mechanical properties of composites can also be predicted by means of micromechanical models. These models are based on different assumptions and experimental data. The most common models are based on the rule of mixtures (ROM), and these models can be used to back calculate the intrinsic properties of the reinforcing fibers [7–9]. In the case of short fiber semialigned composites, the most commonly used models for predicting the Young's modulus are the modified ROM (mROM) [10], the Hirsch model [11], and the Halpin-Tsai equations with Tsai-Pagano methods [7,12–14].

Unlike the tensile stress of the composites, the Young's moduli are not greatly affected by the addition of coupling agents [7].

In this work, composites from PP and orange tree pruning fibers (OPF) were formulated, prepared, and tested to mechanically characterize their Young's modulus. The moduli were analyzed and their micromechanical aspects were evaluated. The stiffening effects of the OPF were compared with SGW from agroforestry [7]. The values of the intrinsic Young's moduli of the fibers were obtained by means of the Hirsch model [11], and the Halpin-Tsai equations with Tsai-Pagano methods [12–14] and then, compared to assess the influence of the aspect ratio on the values. The mean orientation angles of the fibers inside the composite were also computed by means of Cox-Krenchel equations [15,16]. Finally, a fiber tensile modulus factor (*FTMF*) was defined as a way to evaluate, from an industrial point of view, the stiffening capabilities of the reinforcing fibers.

EXPERIMENTAL

Materials

The composites were prepared using PP homopolymer (Isplen PP099 G2M) with a Young's modulus of 1.5 GPa, an average melt flow rate (230°C; 2.16 kg) of 55 g/10 min and a density of 0.905 g/cm^3, of which was provided by Repsol-YPF (Tarragona, Spain). Polypropylene functionalized with maleic anhydride (MAH-PP) (Epolene G3015) with an acid number of 15 mg KOH/g and Mn of 24800Da was acquired from Eastman Chemical Products (San Roque, Spain). The biomass from OPF obtained from seasonal tree pruning was supplied by Mas Clara de Domeny S.L. (Girona, Catalonia, Spain).

Methods

Preparation of Orange Tree Pruning Derivatives. All the biomass from the orange tree prunings was submitted to a crushing and classification process. Some OPF were submitted to a defibering process under cold aqueous conditions in a Sprout-Waldron machine, to obtain MP with a high aspect ratio. The process gave an almost 100% yield with respect to the primary material [17,18]. Other OPF were submitted to a thermo-mechanical process (vaporization followed by defibering). The OPF were heated to 160°C for 30 min, and the resulting pulp was rinsed with water and then passed through a Sprout-Waldron mill, resulting in thermo-mechanical pulp (TMP) with an increased reactant surface, and around a 95% yield. To obtain chemi-thermomechanical fibers, the OPF were submitted to a sodium-hydroxide-antraquinone (AQ) cooking process (5% NaOH: 0.1% AQ) in a liquid to fiber ratio of 4:1, working at 160°C for 20 min. Afterwards, the slurry was washed and shredded using Sprout-Waldron equipment, giving around a 90% yield.

Density Measurement. The density measurement of the composite (ρ^c) was carried out using a pycnometer. Distilled water at 23°C was used as a reference liquid. The ISO 118-3 standard was respected throughout this experiment. The density of the fiber (ρ^f) was obtained from: $\rho^c = \omega^c / \left((\omega^m/\rho^m) + (\omega^f/\rho^f) \right)$, where w^c, w^m, and w^f are the loads in weight of the composite, matrix, and fiber and ρ^m is the density of the matrix.

Compounding, Composite Processing, and Mechanical Characterization. All the processes were carried out in agreement with ASTM D638 standard, and according to the methods described by Lopez et al. [7].

The samples for the tensile test were produced with a steel mould in an injection-molding machine (Meteor 40, Mateu & Solé). Ten test specimens from each obtained composite blend were used for the experiment. The processing temperatures were 175, 175, and 190°C (the machine has three heating areas), the last corresponding to the injection nozzle. First and second pressures were 120 and 37.5 kgf/cm^2, respectively. Standard composite specimen samples (~ 160 × 13.3 × 3.2 mm) were obtained and used to measure the tensile properties.

Prior to the mechanical testing, the specimens were stored in a Dycometal conditioning chamber at 23°C and 50% relative humidity for 48 h, in agreement with the ASTM D638 standard. Afterwards, composites were assayed in a Universal testing machine (Instron™ 1122), fitted with a 5-kN load cell and operating at a rate of 2 mm/min. Young's modulus was analyzed using extensometer in dog-bone specimens. Results were obtained from the average of at least five samples.

Fiber Extraction from Composites

Reinforcing fibers were extracted from composites by matrix solubilization using a Soxhlet apparatus and decalin as solvent. Small pieces of composites were cut and placed inside a cellulose filter and set into the Soxhelt equipment. A small cotton tab was used to prevent the fibers from

TABLE 1. Young's moduli of the MP, TMP and CTMP from OPF/PP composite materials, and reinforcement contributions.

	OPF content $\%^{w}/_{w}$	20% 0,2	30% 0,3	40% 0,4	50% 0,5
MP	V^f	0,153	0,237	0,326	0,420
	E_t^C (GPa)	2,80	3,7	4,35	5,15
	$\eta_e E_t^f$ *(GPa)*	9.99	10.78	10.24	10.19
	$\eta_e E_t^f V^f$ (GPa)	1,53	2,55	3,34	4,28
	l^f (μm)	268	256	241	234
	d^f (μm)	20.1	19.8	19.6	19.7
	ε_t^f (%)	5.2	4	2.8	2.16
TMP	V^f	0,149	0,231	0,319	0,412
	E_t^C (GPa)	2,60	3,10	3,65	4,20
	$\eta_e E_t^f$ (GPa)	8.88	8.43	8.24	8.05
	$\eta_e E_t^f V^f$ (GPa)	1,32	1,95	2,63	3,32
	l^f (μm)	327	310	290	282
	d^f (μm)	19.3	19.4	19.5	19.3
	ε_t^f (%)	5.5	4.3	3	2.61
CTMP	V^f	0,142	0,221	0,307	0,399
	E_t^C (GPa)	2,50	2,94	3,40	4.0
	$\eta_e E_t^f$ (GPa)	8.54	8.01	7.69	7.76
	$\eta_e E_t^f V^f$ (GPa)	1,21	1,77	2,36	3.10
	l^f (μm)	350	331	311	301
	d^f (μm)	19.4	19.6	19.7	19.7
	ε_t^f (%)	5.9	4.6	3.8	3.1

getting out of the filtering tube. The fiber extraction was completed after 24 h. Once the fibers were extracted, they were rinsed with acetone and then with distilled water in order to remove the solvent residue. Finally the fibers were dried in an oven at 105°C for 24 h. [7].

Determination of the Fiber Length and Diameter

Fiber's length distribution and diameter of the extracted fibers were characterized by means of a MorFi Compact (Morfological fiber analyzer), from Techpap SAS, (France). A minimum of two samples were analyzed.

Determination of Young's Moduli of the Fibers. The intrinsic tensile modulus (E_t^f) of the MP, TMP, and CTMP from the OPF was determined using the Hirsch model (Eq. 1) [11,19–21].

$$E_t^C = \beta \cdot \left(E_t^f V^f + E_t^m \left(1 - V^f\right)\right) + (1-\beta)\frac{E_t^f \cdot E_t^m}{E_t^m \cdot V^f + E_t^f (1 - V^f)} \quad (1)$$

Where E_t^C, E_t^f, E_t^m are the elastic modulus of the composite, the reinforcement, and the matrix respectively; and V^f is the volume fraction of the reinforcement. In the model, β is the parameter which determines the stress transfer between the fiber and the matrix. It has been reported that the value of β is mainly influenced by the orientation of the fibers, and by the stress concentration effects at the end of the fibers [22]. A value of $\beta = 0.4$ has been reported to adequately reproduce results obtained experimentally for natural fiber composites [20,23].

Tsai-Pagano model (Eq. 2) and the Halpin-Tsai equations (Eq. 3,4) [13,14] were also used to predict the intrinsic tensile modulus of the fibers. The calculation was made in accordance with Lopez et al. [7]

The stiffness in the fiber direction is given by:

$$E_t^C = \frac{3}{8}E^{11} + \frac{5}{8}E^{22} \quad (2)$$

Here, E^{11} and E^{22} are the longitudinal and transversal elastic modulus, calculated by the Halpin–Tsai equations [24]:

$$E^{11} = \frac{1 + 2\left(l^f/d^f\right) \cdot \eta_l V^f}{1 - \eta_l V^f} E_t^m, \quad (3a)$$

$$E^{22} = \frac{1 + 2 \cdot \eta_t V^f}{1 - \eta_t V^f} E_t^m \quad (3b)$$

Being the parameters η_l and η_t given by:

$$\eta_l = \frac{\left(E_t^f/E_t^m\right) - 1}{\left(E_t^f/E_t^m\right) + 2\left(l^f/d^f\right)}, \quad (4a)$$

$$\eta_t = \frac{\left(E_t^f/E_t^m\right) - 1}{\left(E_t^f/E_t^m\right) + 2} \quad (4b)$$

Where l^f and d^f are the length and the diameter of the ONF.

Differential Scanning Calorimetry (DSC). The crystallization behavior of the composites was investigated by means of a 820-Mettler Toledo differential scanning calorimeter, equipped with a cooling system under nitrogen atmosphere. DSC analysis was conducted from 40 to 250°C with a 10°C/min heating rate [25]. The degree of crystallinity (X_c) was determined with the methods presented by Lopez et al. [25].

RESULTS AND DISCUSSION

Generally, the Young's modulus of the composites depends on the kind of matrix, the type of reinforcement, the degree of the reinforcement dispersion, the intrinsic modulus of the fiber, the percentage of reinforcement, the orientation factor and the aspect ratio (l^f/d^f). Young modulus is not greatly affected by the addition of coupling agents [3,7,26], but this work is part of a series of research into OPF/PP composites and we tested the same composite materials.

The Young's experimentally obtained moduli of tested PP- composite materials reinforced with OPF, are presented in Table 1, where E_t^C is the Young's modulus of the composite, l^f and d^f are the means, weighted length and diameters of the reinforcement fibers, ε_t^f is the strain at composite failure, η_e is the efficiency factor, and V^f is the volume fraction of reinforcement in the composite.

The Young's moduli of the composites increased linearly with the fiber content as a result of the fibers

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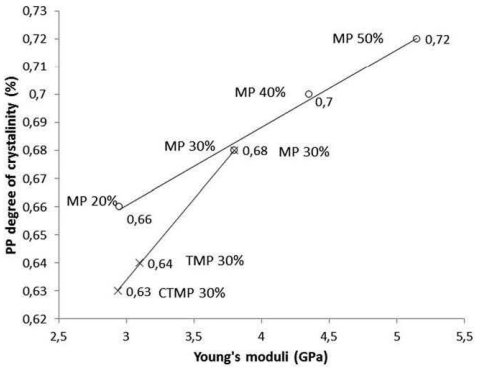

FIG. 1. Polypropylene degree of crystallinity against Young's moduli for the 30 wt% composites.

exerting a resistance against the plastic deformation of the PP matrix, which in turn restricts polymer chain elongation [27]. At the same time, the increase of the moduli suggests an efficient stress transfer between the polymer and the fibers [28]. Looking further into the mechanism that increased the moduli, there are authors who explain that fact by stating that the incorporation of fibers into the thermoplastic increases the moduli because the mobility in the amorphous region becomes increasingly restrained, as the fibers are stiffer than the thermoplastic. Nonetheless, the degree of crystallinity (X_c) of a material is an indicator of its stiffness, and the higher its crystallinity is, the higher its stiffness is. In fact, there are other works based on the increases of Young's modulus on the increasing content of crystalline cellulose or the increasing of the crystallinity index [1,28–30]. In this study, as Young's modulus of the composite materials showed (Table 1) MP composites showed higher stiffness than TMP and CTMP. This fact is shown more clearly in Fig. 1, which shows Young's modulus against treatments. While there is some literature that bases the changes of the mechanical properties of the composite materials on the changes of the diameters of the fibers [31] the MP, TMP, and CTMP fibers from the OPF showed little variations in diameter, with a mean value of 19.6 μm. Neagu [4] obtained higher values for the Young's modulus of CTMP when compared with TMP, and while this may seem to be a contradiction, we lack details on the treatment processes of the fibers and their yields to be able to comment. Results of the DSC experiments (Fig. 1) gave evidence that, as increasing percentages of OPF were incorporated, the matrix X_c increased. It is accepted that cellulosic fibers can act as nucleating agents for crystallization of PP [25,32,33]. Conversely, the intensity of the fiber treatments led to decreases in the matrix X_c. In any case, a high correlation between the matrix X_c and the Young's moduli was found (Pearson's $p = 0.009$). The degree of crystallinity was also measured for the 20 to 50% MP composite materials, and it was observed that X_c evolved linearly from 0.66 to 0.72, thus the increase of the reinforcement fibers increased X_c.

In the present case, the addition of 50% (by weight) of MP, TMP, and CTMP from the OPF in PP, increased the Young's modulus of the plain matrix by a factor of 3.4, 2.9, and 2.7, respectively. With the same amount of MP from SGW a 3.5 increase [7] was obtained, showing that the effect of MP reinforcement fibers from hardwood and softwood on the Young's moduli was similar. Unfortunately, we do not have values for TMP and CTMP from SGW.

The mROM (Eq. 5) [10], is a common micromechanical model to predict the Young's modulus of composite materials.

$$E_t^C = \eta_e \cdot E_t^f \cdot V^f + E_t^m \cdot \left(1 - V^f\right) \tag{5}$$

Where E_t^C, E_t^f, E_t^m are the elastic modulus of the composite, the reinforcement, and the matrix, respectively; and V^f is the volume fraction of the reinforcement. η_e is the efficiency factor used to correct the contribution of semialigned fibers. Taking into account that the experimental measurement of the Young's moduli of the OPF is impossible, due to fiber lengths, then the equation presents two unknown terms, E_t^f and η_e. In any case, the contribution of the fibers to the Young's modulus of the composite material is represented by the term: $\eta_e \cdot E_t^f \cdot V^f$ [7,34] and its value could be easily computed from the mROM. Table 1 shows the value of the contributions. To determine the global contribution of the reinforcements to the Young's moduli of the composite materials, as a function of the fiber content, a *FTMF* [7] was defined isolating the contribution of the fibers to the Young's modulus of the composite in the mROM (Eq. 6). The *FTMF* was defined as:

$$FTMF = \frac{E_t^C - \left(1 - V^f\right) \cdot E_t^m}{V^f} = \eta_e E_t^f \tag{6}$$

The value of $\eta_e \cdot E_t^f$ (Table 1) shows the influence of the reinforcement on the Young's modulus of the composite, which is determined by the slope of linear tendency of graphs in Fig. 2. Thomason [35] defined a similar factor but instead of the efficiency factor (η_e) he used the orientation factor (η_o). The efficiency factor can be expressed as the product of the orientation factor and the length efficiency factor $\eta_e = \eta_o \times \eta_l$. Usually, the η_o is characteristic of the process and the machinery, and η_l is linked to the attrition phenomena that occur during the preparation and manufacturing processes [9]. A direct effect of the attrition is the decrease in the mean length of the reinforcement fibers when the percentage of fiber increases [9,36,37]. Additionally, to compute η_l, fibers are extracted from the matrix to evaluate the mean length and mean diameters. When it uses η_e, the proposed FTMF can be directly evaluated from the data obtained in the stress-strain test without further manipulation of the composite.

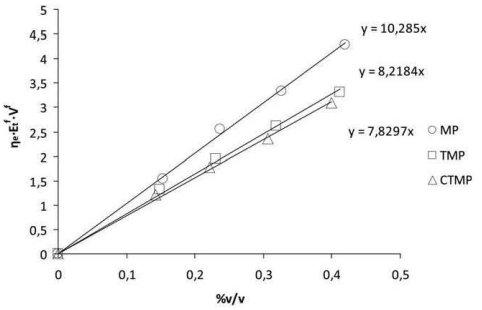

FIG. 2. Fiber tensile modulus factor regression line for MP, TMP, and CTMP from OPF.

In this case, the *FTMF* of MP, TMP, and CTMP from the OPF/PP composites were 10.28, 8.22, and 7.83, respectively. The *FTMF* value obtained by MP from SGW/PP composites [7] was 10.31, very similar to MP from OPF. Conversely, the FTMF of fiberglass/PP composites was evaluated to be 32.68 [7], 3.2, 4, and 4.2 times higher than MP, TMP, and CTMP composites, respectively.

The intrinsic Young's moduli of MP, TMP, and CTMP from the OPF were back calculated by means of Hirsch's model. Table 2 shows the values obtained. The table also shows the values for MP from SGW [19].

The value of Young's moduli of SGW is situated between MP and TMP from the OPF. Neagu et al. [4] determined the Young's modulus of TMP from softwood to be 21.7 ± 4.23 GPa, a value similar to that of MP from OPF.

With the computed values of $E_t^{f_i}$ and by means of the mROM, we calculated the value of the efficiency factors (η_{ej}) (Table 3).

Values of η_e were found to be within the range of 0.5 to 0.53, that is, very similar to that of MP from SGW [7]. Usually, short fiber reinforced polymers present a distribution of fiber length and fiber orientation and so, to consider their influence on the final properties of the composite materials, an orientation factor (η_o) and a length factor (η_l) must be determined and enclosed in the mROM. The length factor was measured according to Cox-Krenchel's model [16]:

$$\eta_l = 1 - \frac{\tan h(\beta \cdot l^f/2)}{(\beta \cdot l^f/2)} \tag{7}$$

With

TABLE 2. Intrinsic Young's moduli of the reinforcement fibers. Data in GPa, standard deviations inside brackets.

	20%	30%	40%	50%	Mean
$E_t^{f(MP)}$	20.28	22.04	20.4	19.83	20.64 (0,96)
$E_t^{f(TMP)}$	17.55	16.22	15.13	14.66	15.89 (1.28)
$E_t^{f(CTMP)}$	16.73	15.24	14.22	14.05	15.06 (1.23)
$E_t^{f(SGW)}$	–	18.9	18.8	17.1	18.2 (1.1)

TABLE 3. Efficiency factors and fiber orientation limit angles computed from the Hirsch model combined with the Cox-Krenchel model, for all tested OPF composite materials.

		20%	30%	40%	50%	Mean
MP	η_e	0.48	0.52	0.50	0.50	0.50 (0.02)
	η_l	0.80	0.82	0.84	0.86	0.83 (0.02)
	η_o	0.60	0.64	0.59	0.58	0.60 (0.026)
	A	46.8°	44.3°	47.8°	49.3°	47.1° (2.1)
TMP	η_e	0.56	0.53	0.51	0.51	0.52 (0.02)
	η_l	0.86	0.87	0.88	0.89	0.88 (0.017)
	η_o	0.65	0.61	0.58	0.56	0.60 (0.039)
	A	43.1°	46.7°	49.1°	50.1°	47.3° (3.1)
CTMP	η_e	0.57	0.53	0.51	0.52	0.53 (0.03)
	η_l	0.87	0.88	0.89	0.90	0.89 (0.015)
	η_o	0.65	0.61	0.57	0.57	0.60 (0.038)
	A	42.9°	46.8°	49.4°	49.6°	47.2° (3.1)

$$\beta = \frac{1}{r}\sqrt{\frac{E_t^m}{E1 \cdot (1-v) \cdot Ln\sqrt{\pi/4 \cdot V^f}}} \tag{8}$$

where β is the coefficient of the stress concentration rate at the ends of the fibers, r is the fiber mean radius, l^f is the fiber's weighted length, v is the Poisson's ratio of the matrix and was assumed to be 0.36 [22], and r is the mean radius of the OPF, being 9.4, 9.2, and 9.3 μm for the MP, TMP, and CTMP, respectively. As mentioned above, the efficiency factor η_e can be expressed as $\eta_e = \eta_o \cdot \eta_l$ and we used the identity to calculate η_l. Table 3 shows the computed η_l and the η_o values.

To calculate the orientation angle, we refer to [38] and [39], who studied the tensile modulus of short fiber reinforced thermoplastics, assuming a rectangular distribution of the fibers inside the matrix (square packing) [7,38], and the orientation efficiency factor was obtained from:

$$\eta_o = \frac{\sin(\alpha)}{\alpha}\left(\frac{3-v}{4}\frac{\sin(\alpha)}{\alpha} + \frac{1+v}{4}\frac{\sin(3\alpha)}{3\alpha}\right) \tag{9}$$

Table 3 shows the computed mean orientation angles for the different composites.

MP, TMP, and CTMP mean fiber orientation efficiency factors were very similar, at around 0.6, which resulted in mean fiber orientation angles around 47.2°. The mean orientation angle, obtained from the orientation factors, when the intrinsic strength of the fibers was calculated [9], was 40.5°. The results may seem contradictory, but in fact the mathematical function that predicts the fiber orientation factor χ_I in the mROM, used to compute the tensile strength, is different from the mathematical function that predicts the orientation efficiency factor (η_o), also in the mROM, used to calculate the modulus. That's clear when $\chi_I \neq \eta_o$.

In addition to the Hirsch model, the Halpin-Tsai equations with Tsai-Pagano methods have long been popular for predicting the properties of short-fiber composites [40]. Moreover the Halpin-Tsai equations account for the lengths and diameters of the strands, while the Hirsch

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model ignores these factors. Thus, in order to find the sensitivity of the Young's moduli prediction against the aspect ratio we computed the intrinsic moduli of the OPF. Table 4 shows the results obtained.

There are small discrepancies between the mean intrinsic moduli computed by the Hirsch model and the Tsai-Pagano equations with the values being 9.9%, higher for MP and 5.8% and 8% less for TMP and CTMP, respectively. Thus, in the case of OPF, the inclusion of the aspect ratio in the determination of the Young's moduli revealed its weight in the determination of the properties. In any case, the value of the FTMF will remain unchanged as it measures $\eta_e \cdot E_t^f$, adding validity to that factor. Logically, if the Young's modulus changes the orientation factor does the same and consequently, so do all the factors. Thus, the process to predict the fiber orientation limit angles was reproduced using the mean intrinsic moduli from Table 4. The mean values are shown in Table 5.

The orientation angles show differences to that on Table 5, with 8.6, 5.9, and 8.3% percentage changes for MP, TMP, and CTMP, respectively, thus revealing the influence of the aspect ratio in the case of OPF.

CONCLUSIONS

OPFs showed competitive Young's moduli values that allow their use for semistructural purposes. That competitiveness is even greater when relative properties are compared.

The degree of crystallinity of the PP matrix considerably affected the value of the Young's moduli of the composite materials. A high inverse correlation between the degree of crystallinity of the matrix and the Young's moduli was detected. It was also found that the increase of the percentage of fibers increased the degree of crystallinity of the matrix, thus positively affecting the stiffness of the materials.

The defined *FTMF* showed its worth in comparing the contribution of the fibers to the final properties of the composite materials. That is more interesting for short fiber semialigned composites where the intrinsic property of the fiber is unknown and impossible to determine experimentally, and the orientation factor is also unknown. The *FTMF* depends on experimental data easily obtained from stress-strain test, and it is not necessary to extract the fibers from the matrix, making it appealing from an industrial point of view.

TABLE 4. Intrinsic Young moduli of OPF fibers computed from Halpin-Tsai equations with Tsai-Pagano methods for all tested OPF composite materials.

	20%	30%	40%	50%	Mean
$E_t^{f(MP)}$(GPa)	24.0	26.2	21.8	19.6	22.90 (2.84)
$E_t^{f(TMP)}$ (GPa)	18.0	15.5	13.8	12.8	15.03 (2.27)
$E_t^{f(CTMP)}$ (GPa)	16.7	14.3	12.7	12.1	13.95 (2.06)

TABLE 5. Efficiency factors and fiber orientation limit angles computed from Halpin-Tsai equations with Tsai-Pagano methods combined with the Cox-Krenchel model for all tested OPF composite materials.

		20%	30%	40%	50%	Mean
MP	η_e	0.44	0.47	0.45	0.45	0.45 (0.02)
	η_l	0.79	0.81	0.83	0.85	0.82 (0.03)
	η_o	0.55	0.58	0.54	0.52	0.55 (0.02)
	A	51.2°	48.9°	52.2°	53.7°	51.5° (2.0)
TMP	η_e	0.59	0.56	0.54	0.54	0.56 (0.03)
	η_l	0.86	0.88	0.88	0.90	0.88 (0.02)
	η_o	0.68	0.64	0.61	0.59	0.63 (0.04)
	A	40.3°	43.9°	46.6°	47.6°	44.6° (3.3)
CTMP	η_e	0.61	0.57	0.55	0.56	0.57 (0.03)
	η_l	0.87	0.88	0.89	0.91	0.89 (0.02)
	η_o	0.70	0.65	0.62	0.61	0.64 (0.04)
	A	39.0°	43.2°	45.9°	46.1°	43.5° (3.4)

The aspect ratio (l^f/ d^f) was needed to solve the Halpin-Tsai equations with Tsai-Pagano methods to predict the intrinsic Young's moduli of the fibers. The final results affected the values, with a 10% maxim discrepancy, predicted by means of the Hirsch model.

The efficiency factors back calculated from the Young's moduli, were placed within the range of 0.5 to 0.6, and were in line with the results obtained with MP from SGW. The orientation efficiency factors were located at around 0.6, which corresponded with a 47.2° mean orientation angle. With MP from SGW, the mean obtained orientation angle was 43°.

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6 ORANGE WOOD FIBER REINFORCED POLYPROPYLENE COMPOSITES: THERMAL PROPERTIES

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Orange Wood Fiber Reinforced Polypropylene Composites: Thermal Properties

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A major drawback of natural-based composites is the incorporation of reinforcements that are less thermally stable than the matrix; therefore, the thermal properties of the resultant composite material needs to be studied. In this work, orange wood fibers were used to reinforce polypropylene. The effects on the thermal properties of the polymeric matrix were analyzed. To this end, differential scanning calorimetry (DSC), thermogravimetry (TGA), thermomechanical analysis (TMA), and dynamic-mechanical analysis (DMA) were performed. It was found that the degradation of the material took place in two distinct phases: the reinforcement, close to 250 °C, and the matrix, above 340 °C. DSC results showed that fiber reinforcement did not influence the transition temperatures of the materials, although it did affect the polymer crystallinity value, increasing by 7% when the composite is reinforced with 50% of the lignocellulosic reinforcement. The coefficient of expansion obtained by TMA indicated that thermal expansion decreased as the amount of reinforcement increased. DMA assays showed that the reinforcement did not modify the glass transition (20 to 25 °C) temperature and confirmed that the addition of reinforcement increased the crystallinity of the product.

Keywords: Polypropylene composites; Orange pruning fibers; Thermal properties

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INTRODUCTION

The use of natural fibers in the reinforcement of thermoplastic polymer-based composite materials can be considered an interesting area of research from different points of view: the production of environmentally friendly materials, valorization of agricultural wastes, and, if the composite is incinerated, lack of solid residue.

Aside from the environmental benefits gained due to better recyclability compared to more rigid fibers, these materials may offer some economic advantages (Lopez *et al.* 2013). Moreover, the comparatively low density of the cellulosic fibers positively affects the specific mechanical properties (Dittenber and GangaRao 2012; López *et al.* 2012b; Reixach *et al.* 2013a).

In the Mediterranean, wood from fruit tree pruning is a huge potential source of cellulosic fibers, which at present is rarely used (Fernández-Puratich *et al.* 2013). In Spain,

residues from citrus orchards amount to about $1.15 \cdot 10^6$ tons per year; in most cases it is burned in the fields, producing CO_2 emissions (Reixach *et al*. 2013b). The use of this residue as a reinforcement for composite materials is a way to increase the value of this byproduct and represents a low cost alternative to natural fibers (Mishra and Sain 2009). Fiber reinforcement of thermoplastic polymers is a common technology, used to improve mechanical properties such as Young's and flexural modulus and the flexural and tensile strength of the composite materials, though it also decreases ductility and impact resistance (Ku *et al*. 2011; Kumar *et al*. 2011). Natural fibers are currently used as a reinforcing material in the automotive, building, packaging, and furniture industries (Neagu and Gamstedt 2007; Julian *et al*. 2012a,b)

To achieve good mechanical properties in the composite, it is important to ensure an adequate fiber dispersion and interfacial compatibility, which requires the use of coupling agents (Liu *et al*. 2014). Mixing hydrophilic fibers with a hydrophobic matrix results in difficult dispersion of the fibers, because of the strong interfiber hydrogen bonding which holds the fibers together (Bigg *et al*. 1988; Lu *et al*. 2000). The use of coupling agents to improve the compatibility and adhesion between polar wood fibers and non-polar polymeric matrices is currently used (Maldas and Kokta 1989).

One of the limitations related with the use of natural fibers is the low range of temperature allowed to process the composite to avoid fiber degradation (López *et al*. 2012a). To avoid this problem, it is important to determine the melting and degradation temperatures of the composite material. It is also necessary to be aware of changes in mechanical behavior as a result of the temperature of the material processing conditions. The objectives of this work were to characterize the degradation temperature and melting temperature of polypropylene reinforced with different amounts of orange fiber, the thermal expansion coefficient and the storage modulus of these composites at different temperatures.

EXPERIMENTAL

Materials

Polypropylene homopolymer (Isplen PP099 K2M, Repsol-YPF, Tarragona, Spain) was used as a polymer matrix with an average melt flow rate (230 °C; 2.16kg) of 55 g/10 min and a density of 905 kg/m^3. Grafted maleic anhydride polypropylene (MAH-PP) (Epolene G3015, Eastman Chemical Products, Spain) with an acid number of 15 mg KOH/g and a Mn of 24800 Da was used as coupling agent. Orange tree pruning fibers (OPF) obtained from seasonal tree pruning were supplied by Mas Clarà de Domeny (Spain). Diethyleneglycol dimethyl ether (Clariant) and decahydronaphthalene (Fisher Scientific) were used as a dispersant and solvent, respectively, without prior purification.

Methods

Raw material conditioning, compounding, and composite processing

OPF was submitted to a crushing, by means of a mill equipped with a set of steel knives, and a classification process using metal sieves, in order to reduce and control the wood pieces size. Later, it was submitted to a de-fibering process under cold aqueous conditions in a Sprout-Waldron refiner, to obtain mechanical pulp (MP) with a high aspect ratio and a yield of almost 100% (Thamae *et al*. 2008; Ashori and Nourbakhsh 2009).

Composite materials comprised of 20 to 50 wt.% PP/OPF, compatibilized with MAH-PP (6 wt.%), were obtained. The components were added and compounded in a Gelimat kinetic mixer, which reached 2500 rpm and discharged the composite at 190 °C. The resulting blends were ground with a knives mill, dried, and stored at 80 °C for at least 24 h before processing.

The samples for characterization were produced by injection-molding (Meteor 40, Mateu & Solé). Ten test specimens from each composite were used for each experiment. The processing temperatures increased from 175 to 190 °C; the highest was that of the nozzle. First and second pressures were 120 and 37.5 kg_f/cm^2, respectively. Standard composite specimen samples (approximately 160 x 13.3 x 3.2 mm) were obtained and used to measure the thermal properties.

Thermal characterisation (TGA/DSC)

Thermogravimetric analysis was performed using a TGA/SDTA 851 Mettler Toledo instrument. The samples were heated from 30 to 700 °C, at a heating rate of 10 °C/min, under an inert atmosphere (40 mL/min of N_2). The equipment was connected to a computer, which registered the evolution of the sample weight against the temperature profiles.

Differential scanning calorimetry was performed using a Mettler Toledo DSC822e thermal analyzer, following ASTM E1269.01 standard specifications. A standard procedure was based on a first heating from 40 to 210 °C, a cooling from 210 to 40 °C and another heating to 210 °C. The three processes were conducted at a controlled heating rate of 10 °C/min in an inert atmosphere (40 mL/min of N_2).

Thermo and dynamical mechanical analysis (TMA/DMA)

Thermomechanical analysis was performed using a Setaram Setsys Evolution 16 instrument under compression stress, according to ASTM E831 standard specifications. To ensure good contact, a force of 5 g was applied to the samples. The samples were heated from 30 to 120 °C, at a heating rate of 3 °C/min, in an inert atmosphere (40 mL/min of N_2).

The samples were assayed using a Mettler Toledo DMA/SDTA 861 instrument by setting the following conditions: preload of 3N, frequency of 1Hz, and heating from 30 to 120 °C at a rate of 3 °C/min. The experiments were conducted in an air atmosphere.

RESULTS AND DISCUSSION

Thermogravimetric Analysis (TGA)

The results of the thermogravimetric assays are represented in Fig. 1. The TGA of the neat matrix showed a single degradation step, starting at 345 °C. This step can be attributed to PP, which led to the complete degradation of the material without leaving any noticeable residue. The evolution of weight loss in fiber-reinforced composites also followed the typical patterns for this kind of material (López *et al*. 2012a; Gwon *et al*. 2014). Cellulose, as well as the residual lignin remaining in the fibers after being submitted to the thermo-chemical treatment (Reixach *et al*. 2013b), starts to degrade at about 250 °C (Espigulé *et al*. 2013). For composites comprised of 20 to 30% fiber content, this phenomenon resulted in a clear two-step degradation curve. For materials with higher fiber content, these two degradation sequences were partially overlapped, although both can be clearly seen in the DTGA curves (Fig. 2).

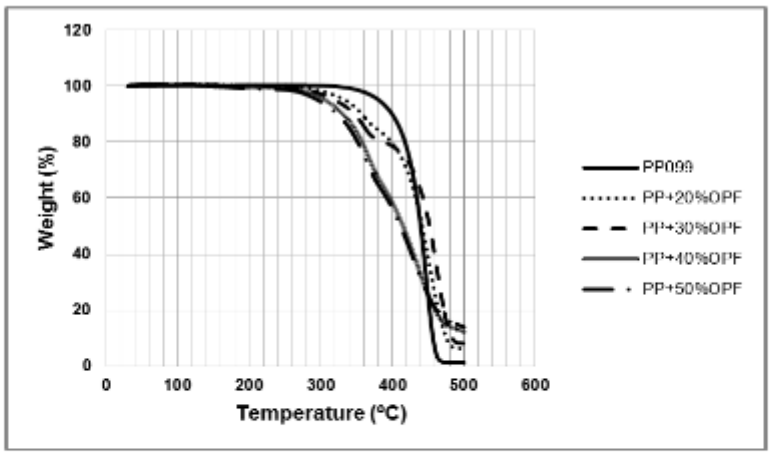

Fig. 1. TGA of 20 to 50 wt.% OPF reinforced PP composite materials

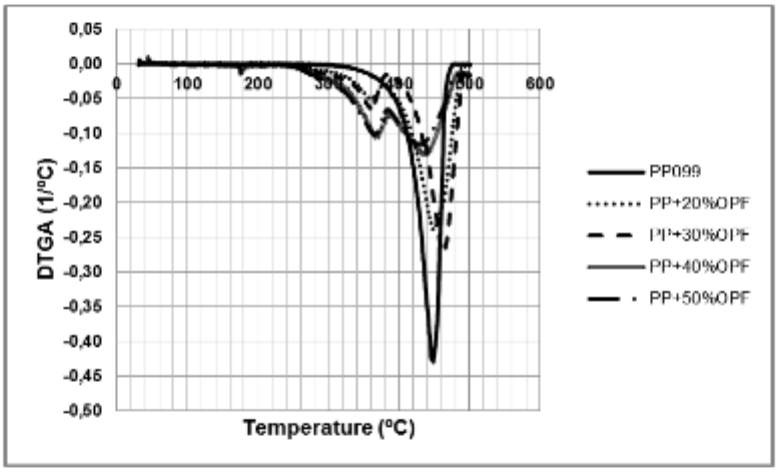

Fig. 2. DTGA of 20 to 50 wt.% OPF-reinforced PP composite materials

The thermal degradation processes of OPF reinforcement started at about 250 °C and were not affected by the fiber content. The end of the OPF degradation curve overlaps the polymer degradation curve; hence, it does not allow for the determination of the starting point of such a process. Nevertheless, the peaks of the DTGA curves were not affected by the composition of the reinforcement, suggesting independent processes.

Table 1 summarizes the initial degradation temperatures and weight losses of each degradation process, as well as the ultimate residual contents. As shown in the table, the weight loss in the TGA curves did not match the reinforcement weight content. This difference is related to the partial overlapping of the two main degradation steps. However, it might also be caused by deficient fiber dispersion within the composite, by the accumulation of reinforcing fibers in some specific areas of the composite (Kim *et al.* 2013), or even by deficient sampling if the core/skin effects had not been taken into consideration.

Table 1. Summary of the Properties Obtained from Figs. 1 and 2

Composition	Tonset1 (°C)	1st loss of weight (%)	Tonset2 (°C)	2on loss of weight (%)	Residue (%)
PP	-	-	345.6	95.2	1.3
PP+OPF 20%	254.2	15.8	370.3	75.1	5.7
PP+OPF 30%	244.7	19.6	369.5	71.8	7.6
PP+OPF 40%	251.7	34.9	372.1	52.2	12.3
PP+OPF 50%	245.3	36.3	378.3	47.2	13.9

Differential Scanning Calorimetry (DSC)

The main results of the DSC tests are presented in Table 2.

Table 2. Thermal Properties of the Composites Reinforced with Cellulosic Fibers Produced from Orange Tree Prunings

Composition	Fusion Temperature (°C)	Crystallization Temperature (°C)	Crystallization Enthalpy (J/g PP)	Crystallization (%)
PP	163.7	124.6	106.3	55.9
PP+OPF 20%	165.5	125.9	109.1	57.4
PP+OPF 30%	167.1	124.5	109.1	57.4
PP+OPF 40%	167.9	123.3	112.0	58.9
PP+OPF 50%	166.3	124.4	113.7	59.8

The fusion and crystallization temperatures correspond to the minimum/maximum, respectively, of the DSC curves shown in Figs. 3 and 4. Results demonstrate that the reinforcing fibers did not significantly affect the melting/crystallization processes of the PP matrix.

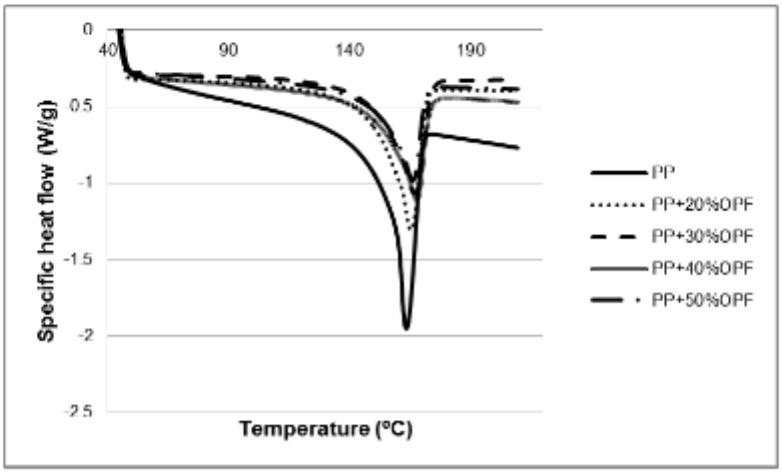

Fig. 3. Graphical comparison of the melting endotherm of the matrix and the fiber-reinforced orange wood

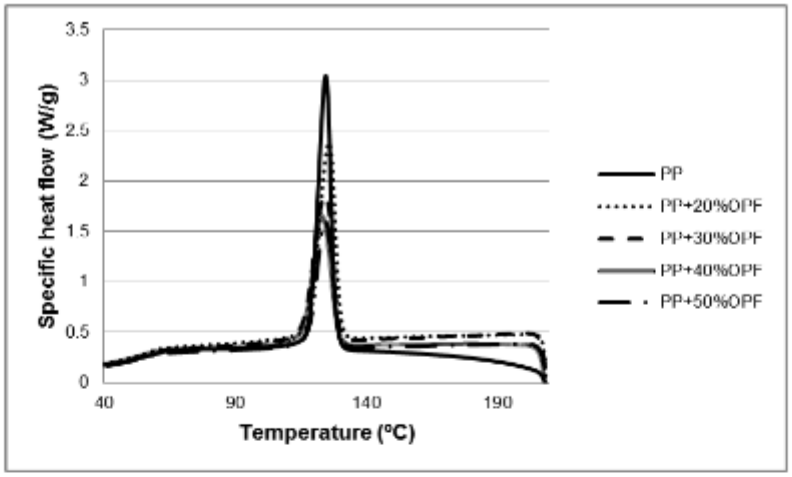

Fig. 4. Graphical comparison of the crystallization exotherm of the matrix and the fiber-reinforced orange wood

Thus, it can be concluded that there was no significant variation in either the melting or crystallization temperatures of the composites. In addition, once the area under the DSC curves was corrected to account for the amount of matrix present in each composite, only a slight increase could be detected in the crystallization degree versus the reinforcement content. Although not clearly significant, this increase could be related to fibers acting as nucleating agents (Amash and Zugenmaier 2000).

Thermo-Mechanical Analysis (TMA)

The coefficients of thermal expansion were determined by TMA, with the results reported in Fig. 5.

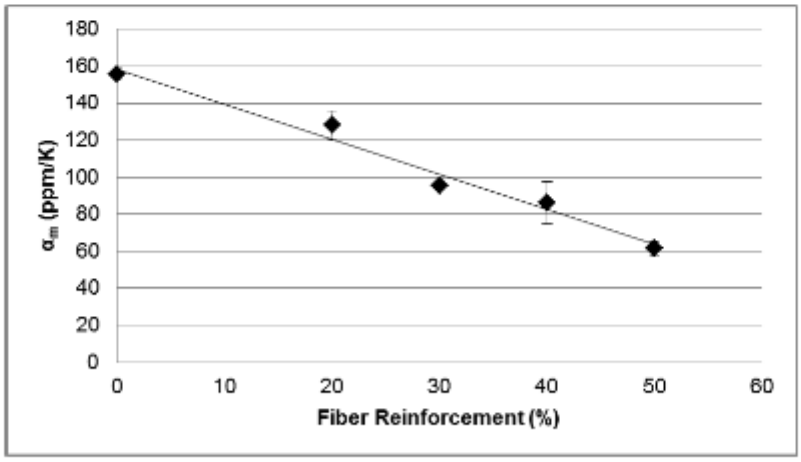

Fig. 5. Coefficient of thermal expansion as a function of fiber content

The thermal expansion coefficients showed a progressive diminution with increasing reinforcement content, which agrees with the minimal thermal expansion of

cellulosic fibers compared to the PP matrix (Rukmini *et al*. 2013). Thus, as could be expected, the thermal expansion coefficient diminished from 155 $\mu m \cdot m^{-1} \cdot K^{-1}$ for neat PP to 61 $\mu m \cdot m^{-1} \cdot K^{-1}$ for composites with 50% fiber content.

Dynamic-Mechanical Analysis (DMA)

The viscoelastic behavior of the composites was analyzed by DMA. The results are summarized in Figs. 6 and 7. The storage modulus curves show the typical pattern for thermoplastic materials, with a progressive rigidity loss as the temperature increases. A comparison between composites evidences the effect of the reinforcing fibers on the rigidity of the materials, as storage modulus increased with rigid fiber content.

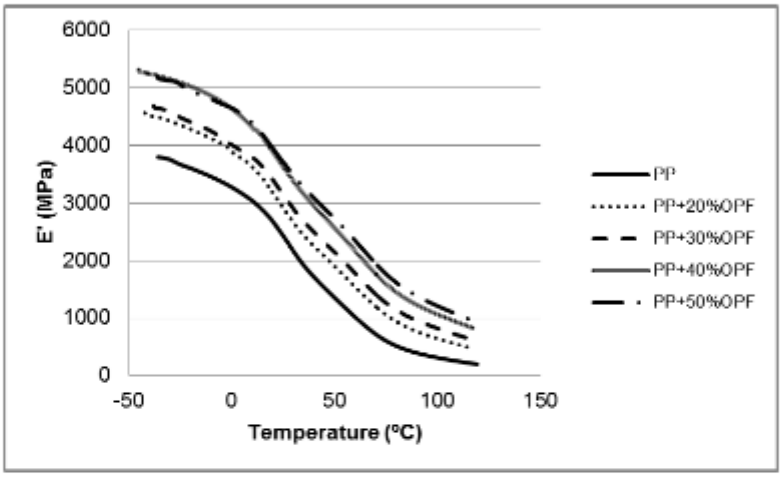

Fig. 6. Storage modulus of PP and PP composites reinforced with orange fiber

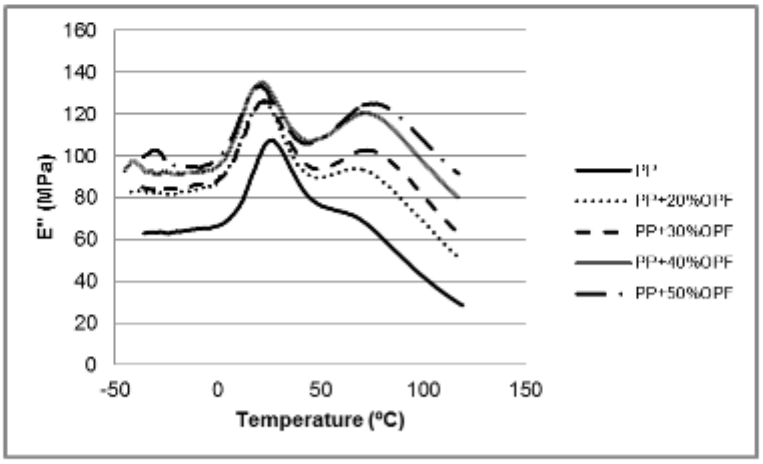

Fig. 7. Loss modulus of PP and PP composites reinforced with orange fiber

Regardless of fiber content, the loss modulus curves present a peak at about 10 to 30 °C assigned to the glass transition temperature (T_g) of PP. Although this temperature range is greater than expected for PP, which was between -10 and 0 °C when determined by DSC (Farzaneh and Tcharkhtchi 2011), it is commonly admitted that DMA reports

greater values for glass transition temperature (Rahman *et al*. 2007). In Table 4 it can be seen that there was a slight influence on the transition temperature by the fiber reinforcement.

In Fig. 7, a second peak at 60 to 80 °C can also be observed, demonstrating that peak intensity and position were affected by the reinforcement content. Literature suggests that these signals are a result of molecular rearrangements within the crystalline phase of the polymer, although it is not clear if they are due to the movement of amorphous sections entrapped within a crystalline section (Rosa *et al*. 2009; Sarlin and Immonen 2013), crystalline rotation (Amash and Zugenmaier 1998), or lamellae displacements (Amash and Zugenmaier 1998; Quan *et al*. 2005). Nevertheless, the increase in this peak temperature can be related to the crystalline fraction of the composite, and this phenomenon agrees with the results obtained by DSC.

Table 4. Temperatures at which the Thermogram of the Loss Modulus Exhibits Its Maximum Values

Composition	T_g	$T_{peak}2$
PP	25	-
PP+OPF 20%	25.6	63.4
PP+OPF 30%	25.6	70.5
PP+OPF 40%	21.4	69.8
PP+OPF 50%	20.7	76.9

CONCLUSIONS

1. Results of the TGA tests showed that the materials reinforced with lignocellulosic fibers from orange pruning exhibited two degradative steps that corresponded to the characteristics of the PP and the fiber.
2. The presence of lignocellulosic fibers caused no changes in the temperatures at which the major transitions of the polymer phase occurred: glass transition, crystallization, and melting. However, the incorporation of lignocellulosic fibers increased crystallinity, as shown by DSC and DMA tests, so it can be concluded that the fibers acted as a nucleating agent.
3. The thermal expansion of the composites decreased as the amount of reinforcement increased. This result was due to the lower coefficient of expansion of the reinforcement compared to that of the matrix.
4. The addition of a reinforcement material stiffer than that of the matrix caused an increase in storage modulus. This property decreased with the temperature of the material.

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7 ACOUSTIC PROPERTIES OF AGROFORESTRY WASTE ORANGE PRUNING FIBERS REINFORCED POLYPROPYLENE COMPOSITES AS AN ALTERNATIVE TO LAMINATED GYPSUM BOARDS

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Acoustic properties of agroforestry waste orange pruning fibers reinforced polypropylene composites as an alternative to laminated gypsum boards

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HIGHLIGHTS

- Agroforestry waste orange tree pruning are used as reinforcement.
- The tested composites showed better insulation than common solutions.
- The tested materials are due to be used as light sound insulation solutions.

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ABSTRACT

The present paper investigates the acoustic properties of natural fiber reinforced composites. Fibers from orange tree pruning were obtained and subject to different treatments in order to obtain mechanical, thermomechanical and chemi-thermomechanical pulps. These pulps were used as reinforcement for a polypropylene matrix. The obtained composite materials were submitted to acoustical tests in an impedance tubes device. The transmission losses obtained against the fiber content were obtained and discussed. Latter it was researched the influence of the fiber treatments on the soundproof characteristics. A numerical method was used to preview the acoustic insulation of the materials against the sound frequency. Finally the results were compared with that of the most usual lightweight soundproof solutions.

1. Introduction

Noise is considered one of the worldwide biggest polluters [1,2]. In the 90s, the World Health Organization (WHO) provided worrying data about that kind of pollution in the United States: about 40% of the population were exposed to road traffic noise with an equivalent sound pressure level exceeding 55 dB(A) daytime and 20% were exposed to levels exceeding 65 dB(A). More than 30% were exposed at night to equivalent sound pressure levels exceeding 55 dB(A) which is disturbing to sleep. In the recent decades, the society progressed significantly, from industrial, technological and social points of view. Most of the actions made by the human beings in relation with the industry, the use of new technologies, or in their day to day interactions with the environment are a cause of noise. Therefore, noise pollution remains a matter to be resolved. The effects on the health due to noise exposure are well known [3]. Most health effects are of a sensorial kind as stress, leading to high blood pressure, coronary heart disease, stroke, and other. In most cases the diagnosis is not immediate, aggravating the situation further. Sound insulation is one of the techniques used to reduce the effects of noise in the cited cases. However, the problem is not completely solved and needs further research to find new materials capable of improving the performance of the conventional solutions [4–6]. In the case of buildings, the most used solutions are light materials as the laminated gypsum boards. Construction materials as lightweight aggregate concrete have been researched and its acoustic properties have been characterized [7,8], but, to the best knowledge of the authors, the proposed agroforestry waste reinforced composites have been not studied.

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On the other hand, there is a need for new and innovative materials capable to satisfy new requirements as lightness, sustainability and cost efficiency [9–12]. Composite materials are a very active research field, and the source of many engineering solutions. As an example, natural fiber reinforced composites provide a way to recover and add value to agro-forestry wastes, avoiding its incineration and the resulting generation of CO_2. For this research, the use of orange tree pruning as reinforcement for composite materials can reduce the need for burning, provide low cost alternatives to wood fibers, and extend the value chain for the agricultural industry [13].

The main advantages of using lignocellulosic fibers, instead of mineral fibers, as reinforcement of polyolefin matrices are; their high specific mechanical properties, good aspect ratios, low equipment abrasion during preparation and manufacturing, high availability, low density, and comparatively low cost per volume basis [14]. The last of the potential advantages is clear, as orange tree pruning are agro-forestry wastes with any value. Moreover, the composite materials reinforced with natural fibers, as orange tree pruning, could be considered almost 100% recyclable, as recovering energy by incineration is possible.

In many of the States of the European Union the basic quality soundproofing levels that all the buildings and installations must achieve are regulated. Hence, all the proposed solutions must be adapted to these regulations. The norms include materials and procedures to correctly obtain the targets, as well as the tests to be performed, to prove the quality of the results. While some of the regulations are informative, some others are mandatory, setting bounds for the insulation, limit values for the reverberation time and installation vibrations. The energy savings must be also noted, having in account the guidelines to obtain buildings with an envelope that limits the energy demands to obtain a correct thermal comfort. Moreover, Directive 89/106/CEE-construction products, and Regulation UE no. 305/2011, that is applicable from July 2013 and must be developed by the member countries, adds in one of the annexes the regard to the use of sustainable and natural resources. The annex establishes that new building works must be designed, build and demolished in a way that the use of natural resources is sustainable and ensure: (a) the reuse and recycling of all the materials after the building is demolished, (b) the durability of the building and (c) the use of raw materials and secondary materials must be compatible from an environmental point of view. In that context it is possible to propose real sound-proofing solutions, based on the studied composite materials, with application to new building works and to building rehabilitations.

In this work, mechanical pulp (MP), thermomechanical pulp (TMP), and chemi-thermomechanical pulp (CTMP) from orange tree pruning were used to prepare composite materials, formulated with a 20–50 wt% of MP, TMP, and CTMP as reinforcement of a polypropylene (PP) matrix. The acoustic properties, against aerial noise, of single layer soundproof elements made with the formulated composites are tested and discussed. The objective of the research is finding the influence of the percentage of reinforcement on the acoustic properties of the composite materials. It was also researched the influence of the chemical treatments on such properties. The researched materials showed themselves light and feasible solutions for soundproofing against aerial noise, and a clear alternative to the conventionally used laminated gypsum boards.

2. Materials and methods

2.1. Materials

The composites were prepared using polypropylene (PP) homopolymer (Isplen PP099 G2M) with an average melt flow rate (230 °C; 2.16 kg) of 55 g per 10 min and a density of 0.905 g/cm^3, kindly provided by Repsol-YPF (Tarragona, Spain). Polypropylene functionalized with maleic anhydride (MAH-PP) (Epolene G3015) with an acid number of 15 mg KOH/g and Mn of 24,800 Da was acquired from Eastman Chemical Products (San Roque, Spain). Biomass from orange tree pruning fibers (OPF) obtained from seasonal tree pruning was supplied by Mas Clara de Domeny (Girona, catalonia, Spain). Other reactants were used: diethyleneglycol dimethyl ether (diglyme) was supplied by Clariant and was used as dispersing agent. Decahydronaphthalene (decalin) (190 °C boiling point, 97% purity) supplied by Fisher Scientific was used to dissolve the PP matrix in the fiber extraction from composites process. The reactants that were used for fiber treatment are summarized as follows: sodium hydroxide (Merck KGaA, Darmstadt, Germany), anthraquinone (Badische Anilin & Soda Fabric AG, Germany) used without any further purification. Pes-Na (polyethene sodium sulfonate) is an anionic polyelectrolyte. Poly-DADMAC (polydimethyl diallyl ammonium chloride) is a cationic polyelectrolyte. Pes-Na 0.001 N and Poly-DADMAC 0.001 N were supplied by BTG Instruments GmbH (Germany).

2.2. Preparation of orange tree pruning derivatives

All the biomass from orange tree pruning was submitted to a crushing and classification process. Some OPF samples were submitted to a defibering process under cold aqueous conditions in a Sprout-Waldron equipment to obtain mechanical pulp (MP) with a higher aspect ratio. This process gave almost 100% yield with respect to the starting material [15,16]. Another OPF sample was submitted to a thermo-mechanical process (vaporization followed by defibering). The OPF were heated to 160 °C for 30 min, and the obtained pulp was rinsed with water and then passed through Sprout-Waldron equipment, resulting in thermo-mechanical pulp (TMP) with an increased reactant surface, and around 95% yield. For OPF chemi-thermo-mechanical fibers, the OPF were submitted to a sodium/hydroxide/antraquinone (AQ) cooking process (5% NaOH:0.1% AQ) in a liquid to fiber ratio of 4:1, working at 160 °C for 20 min. Afterwards, the slurry was washed and shredded in Sprout-Waldron equipment, giving around 90% yield.

2.3. Compounding

Composite materials comprising 30–50 wt% PP/OPF with and without coupling agent were obtained. The materials were prepared in a Brabender® plastograph internal mixing machine. The working parameters were 80 rpm for OPF during 10 min at a temperature of 180 °C. In the case of the coupled composites, the MAH-PP was added to the plastograph with the PP pellets. The resulting blends were ground with a knives mill, dried, and stored at 80 °C for at least 24 h before processing. Materials with 30–50 wt% MP from OPF where prepared and will be referred in the text as MP a%, were a% is the OPF content. Similarly composite materials with a 30 wt% of TMP and CTMP from OPF were obtained.

2.4. Composite processing

The samples for the tensile test were produced with a steel mold in an injection-molding machine (Meteor 40, Mateu & Solé). Ten test specimens from each obtained composite blend were used for the experiment. The processing temperatures were 175, 175, and 190 °C (the machine has three heating areas), the last corresponding to the injection nozzle. First and second pressures were 120 and 37.5 kgf/cm^2, respectively. Standard composite specimen samples (7 approx. 160 × 13.3 × 3.2 mm) were obtained and used to measure the tensile properties in agreement with ASTM D638.

2.5. Mechanical characterization

Prior to the mechanical testing, the specimens were stored in a Dycometal conditioning chamber at 23 °C and 50% relative humidity for 48 h, in agreement with the ASTM D638 standard. Afterwards, composites were assayed in a Universal testing machine (InstronTM 1122), fitted with a 5 kN load cell and operating at a rate of 2 mm/min. Tensile properties were analyzed by means of dog-bone specimens, according to the ASTM D638 standard. The Young's modulus was obtained with an extensometer. Results were obtained from the average of at least 5 samples.

2.6. Acoustic characterization

The acoustic characterization of the materials is a fast growing research line, mainly due to the expanding services that many companies are required to provide. Some examples are the textile, paper and composite materials industries.

One of the main acoustic parameters to characterize is the specific flow resistance of the composite materials. There are international norms that provide guidance to measure that parameter (ISO 9053:1991), and as an alternative there are also widely accepted experimental procedures [17]. The procedure is based on measurements in an impedance tube, as one of the methods to measure the absorption coefficient at normal incidence, described by the cited norm [18], a parameter of high interest to acoustically characterize the materials as absorbent. However there are no standard procedures to estimate the transmission losses in

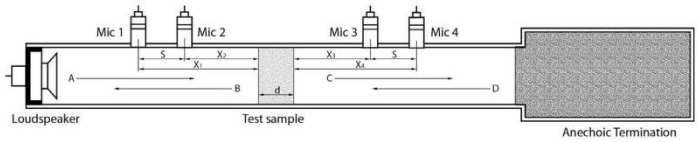

Fig. 1. Diagram of the device used to measure the transmission losses.

Table 1
Main characteristics of the tested specimens.

Material	Young's modulus E (GPa)	Thickness (mm)	Mass (kg/m^2)	Critical frequency (Hz)
MP 20%	2.8	15	14.8	2372
MP 30%	3.7	15	14.8	–
MP 40%	4.3	15	14.8	–
MP 50%	5.1	15	14.8	–
TMP 30%	3.1	15	14.8	2600
CTMP 30%	2.9	15	14.8	2687

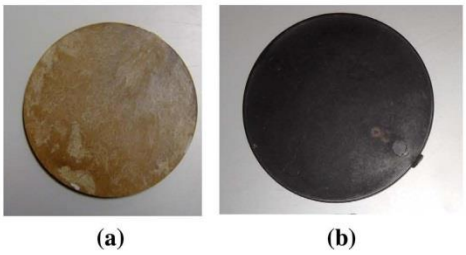

Fig. 2. Visual aspect of the specimens for the (a) 20% and (b) 50% fiber contents.

materials or panels from the impedance tubes. Nonetheless there are some authors that based their measurements of the transmission losses, and their acoustic characterization of the materials, from impedance tubes tests [19–23].

In the Polytechnic School of Gandia, a new method to measure the transmission losses (TL), based on impedance tubes, was developed and used for that research. The design and development was based on the available literature.

The device is based in two impedance tubes used to measure the transmission losses (Fig. 1).

The loudspeaker, placed at the end of the tube, generates plane waves. The path followed by these plane waves inside the tube are referenced in Fig. 1 as A–D the microphones, two placed in the tube between the loudspeaker and the sample, and two placed at the rear end, between the sample and an anechoic termination. The device represents the description of the transference matrix that represents the incident and reflected waves from the upper and lower pats of the sample. If the matrix coefficients are known it is possible to obtain the TL from Eq. (1):

$$\mathrm{TL} = 20\log_{10}\left|\frac{e^{jkS} - H_{12}}{e^{jkS} - H_{34}}\right| - 20\log_{10}|H_t| \tag{1}$$

where S is the distance between the microphones, H_{12} and H_{34} represent the transference function between the microphones 1 and 2 (preceding the sample), and 3 and 4 (subsequent to the sample) respectively, defined by Eq. (2):

$$H_{ij+1} = P_{i+1}/P_i \tag{2}$$

where P_i is the complex acoustic pressure at point i, and is measured by the microphones.

The relation between the auto spectrums, H_t is defined by the Eq. (3):

$$H_t = \sqrt{|S_d/S_u|} \tag{3}$$

where S_u is the auto spectrum preceding the sample and S_d is the auto spectrum subsequent to the sample, that are obtained by applying Eqs. (4) and (5):

$$S_d = P_3 \cdot P_4^* \tag{4}$$

$$S_u = P_1 \cdot P_2^* \tag{5}$$

where P_2^* and P_4^* are the complex conjugates of the complex acoustic pressure at points 2 and 4.

There are some particularities that define the test facility designed at the Polytechnic School of Gandia. The tube preceding the sample measures 1315 mm, and the section subsequent to the sample measures 1233 mm. Both tubes have a 40 mm interior diameter. The distances X_1 and X_2 were 120 and 80 mm, respectively, and X_3 and X_4 120 and 80 mm subtracting the sample thickness. The prototype allows for tree different distances between the microphones, while the standard mechanisms allow only two. The distance between the microphones determines the spectrum of frequencies to measure, as it must be ensured a plane propagation wave in the tube (ISO, 1998). In that work, a 32 mm distance was used to perform all the measures.

2.7. Prediction of the acoustic insulation

There are a lot of models to predict the acoustic insulation, both for aerial and impact sounds [24–28]. Many models used to describe the airborne insulation are based on the coupling effect between the acoustic impedances of the layers of a

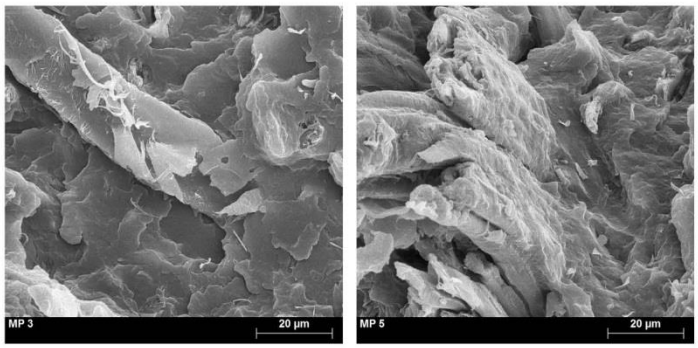

Fig. 3. Visual appearance of the composites and microphotography of the fracture zone in a tensile strength specimen.

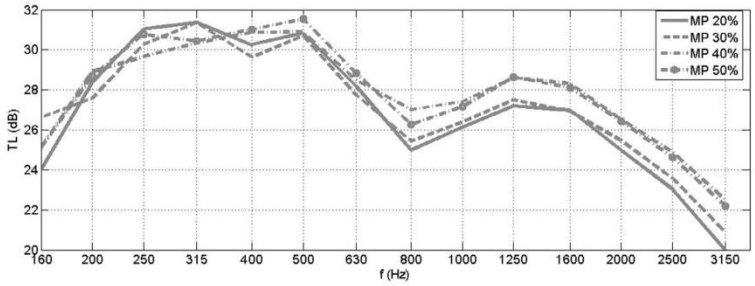

Fig. 4. Transmission loss against the frequency for the 20–50% mechanical pulp polypropylene reinforced composite materials.

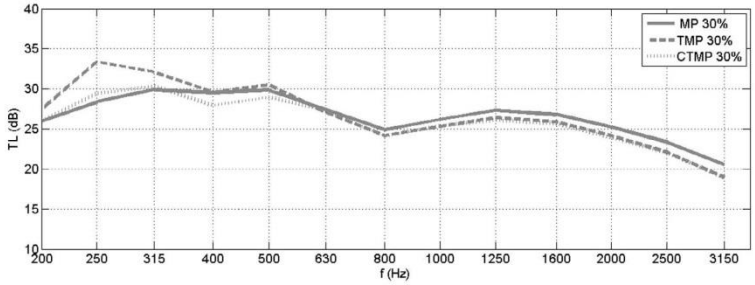

Fig. 5. Transmission loss against the frequency for the 30% mechanical, thermomechanical and chemi-thermomechanical pulp polypropylene reinforced composite materials.

composite to obtain the global isolation of all the layers. The result is the index of sound reduction (R) or the transmission loss (TL) (ISO 10140-2, 2010) (ASTM E90-09), that could be expressed as a function of the frequency or as a global value.

3. Results and discussion

Table 1 shows the main mechanical properties of the composites, used to perform the acoustic insulation calculations. A 15 mm gypsum board has a 10–12 km/m^2 mass, being slightly lighter than the proposed composite materials.

All the tested composite materials showed airflow resistance values higher than 1000 kPaS/m^2. The airflow resistance is the resistance experienced by air as it passes through a material. This property is directly related to the capacity of the material to absorb o reflect sound energy. The high values for the airflow resistance shown by the researched composites imply that such materials act as a sound impervious layer.

The materials showed a toasted color as the amount of reinforcement was increased (Fig. 2).

Likewise, the microphotography of the fracture zone shows the good interface between the fibers and the matrix. The material is compact and not porous, as the matrix totally wets the fibers (Fig. 3).

Fig. 4 shows the transmission loss measured in the tested 20–50 wt% MP composite materials.

Fig. 5 shows the transmission loss or insulation versus the frequency. All the values were obtained under incidence normal conditions. The test were performed in the impedance tube defined in Section 2.

The results are similar for the 20–50 wt% MP from OPF composite materials. Nevertheless, in the case of higher sound frequencies, the composite materials with 40–50 wt% of MP from OPF showed higher values of sound insulation. In the case of mid to low frequencies, the values are similar for all the tested composite materials. That range of mid to low frequencies are the most interesting to have in account as are the most difficult to attenuate. Having that in account it was decided to continue the test with the composite materials with 30 wt% OPF contents. Consequently, MP 30%, TMP 30% and CTMP 30% composite materials were prepared ant tested. Fig. 3 compares the transmission loss measured for the 30 wt% MP, TMP and CTMP composite materials.

In the case of the tested materials, the value of the transmission loses (TL) are very similar, regardless of the fiber treatment. Only the TMP 30% showed higher values for some frequencies.

Fig. 6a and b shows the value of the index of sound reduction that are the result of the numeric simulation. The calculations were made for the 30 wt% MP, TMP and CTMP composite materials, and were compared with that of a lightweight common insulation material (laminated gypsum boards). Two different simulations were made, one supposing a constant thickness for all the samples (Fig. 3b), and the other presuming that the mass of all the samples was the same (Fig. 4b).

The thickness was presumed to be of 13 mm and the mass of 13.1 kg/m^2.

The values for the transmission loss or insulation shown in Fig. 4 were obtained under diffuse field conditions. The numerical methods that allow obtaining the values require an integration limit angle [29]. The influence of the limit angle on the precision of the computed values is an issue of current interest. The limit angle that was used to obtain the values shown in Fig. 4a and b was 78°. It was found that all the tested materials showed a sharp decrease of the insulation property between 2000 Hz and 3000 Hz. These values match the critical frequency, obtained from the mechanical characterization (Table 1).

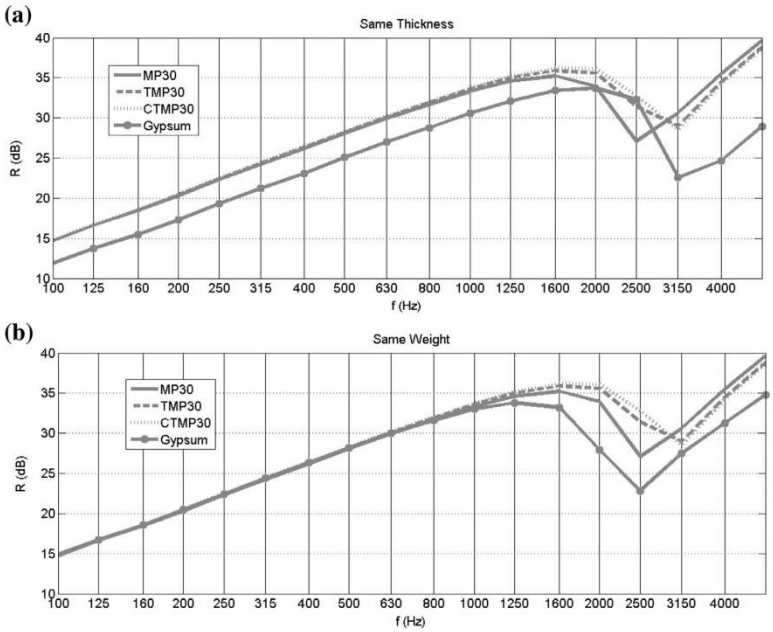

Fig. 6. Numeric simulations of the index of sound reduction for the 30% mechanical, thermomechanical and chemi-thermomechanical pulp polypropylene reinforced composite materials, compared with laminated gypsum boards. (a) constant thickness, (b) constant mass.

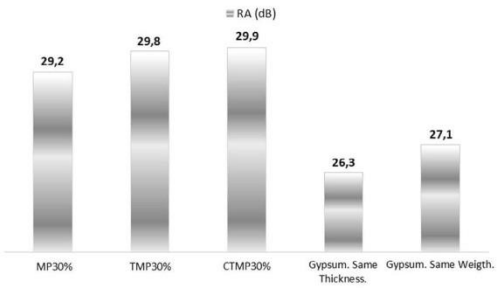

Fig. 7. Acoustic insulation, global values comparison.

The weighted airborne sound insulation values are compared in Fig. 7.

The global values of the evolution show that all the tested composite materials had higher sound attenuation index that that of the commonly used insulation materials. The values are 3 dB higher in the case of the same thickness specimens, and 2 dB higher for the case of same mass specimens.

4. Conclusions

In this work, orange tree pruning fibers reinforced polypropylene composites are presented as airborne insulation solutions. The study presents the behavior of the acoustic properties of such composites against aerial sound. Their mechanical properties, together with their relative lightness and their soundproofing properties, show similarities to that of the impermeable layers, like the laminated gypsum boards, commonly used by builders.

The influence of the reinforcement contents against the acoustic properties was investigated. Reinforcement contents between 20% and 50% were tested. Likewise, it was investigated the incidence of the fiber treatments in the acoustic properties. While the treatments impacted the mechanical properties only showed a slight incidence on the acoustic properties.

Moreover, the obtained insulation properties of the composites are compared with that of the laminated gypsum boards, commonly used as lightweight solution for building. The values were compares by frequencies and by weighted. To obtain this values, a mathematical prediction model was used. The model allowed obtaining the sound reduction index (R) in the diffuse field, understood as random incidence.

The tests developed by using an impedance tube, to investigate the impact of the reinforcement content, showed that by increasing the percentage of reinforcing fibers, the insulation could increase by 2 dB. The transmission loss increased significantly with reinforcement percentages higher that the 20%, mostly for the medium and high frequencies. It was found that for reinforcement contents higher than the 40–50% the soundproofing remained saturated

Composites reinforced with a 30% of MP, TMP and CTMP fibers were submitted to test in the impedance tube. The results showed that the fibers treatment had little influence in the sound insulation properties.

Predictive models were used to compare the acoustic properties of the composites with that of the laminated gypsum boards. Regardless of considering equal mass or equal thickness samples, the soundproofing properties, against aerial sound, of the orange

tree pruning fibers reinforced composites were always superior to that of the laminated gypsum boards. Similarly, when comparing the weighted value, the composites showed properties from 2 to 3 dB higher than that of the laminated gypsum boards.

The mechanical properties of the composite materials, together with the obtained sound insulation properties, make those materials due to be used as light insulation solutions. The application this new material is especially interesting for buildings, but it is possible to use such materials in other fields, as cars or product design.

It will be necessary to perform a lifecycle assessment to study the environmental impact of the agroforestry waste reinforced PP as light insulation solutions, in comparison with laminated gypsum boards, to find if its recyclability compensates the energy need to obtain the raw materials.

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CAPÍTOL IV

CONCLUSIONS GENERALS I FUTURES LÍNIES DE RECERCA

8 CONCLUSIONS GENERALS

Les conclusions de la tesi són les que es presenten als articles publicats, i reflecteixen l'acompliment progressiu dels objectius de la recerca. D'aquesta manera, una vegada publicat el primer article es varen treballar els primers 3 objectius de la tesi. Així doncs, la capacitat de reforç de les fibres es va fer palesa al fabricar i testejar les primeres mostres dels materials compostos, trobant que:els tractaments utilitzats per obtenir pasta mecànica (MP), termomecànica (TMP) i químico-termomecànica de polpa (CTMP) a partir de fibres de poda de taronger van produir canvis en la composició química de les superfícies de les fibres . A la vegada, i paral·lelament als canvis observats en la composició química es va observar que la resistència a la tracció va ser superior amb el compòsit CTMP en relació al MP, no obstant el rendiment del procés disminueix. En el mateix article es va optimitzar la interfase entre les fibres i la matriu, donant resposta al segon objectiu de la recerca. Es va establir un percentatge òptim del 6% de MAPP per les MP i TMP i d'un 4% per les CTMP. En el mateix article es varen estudiar i establir els principals paràmetres micromecànics de la resistència a tracció, responent a part del 3r objectiu de la tesi obtenint els valors de la resistència intrínseca de les fibres, el factor d'orientació i la resistència interfacial.

Una vegada optimitzada la interfase es va estudiar, al segon article, l'efecte dels percentatge de fibra en les propietats a tracció, així com l'efecte dels tractaments de les fibres en les propietats. D'aquesta manera es va poder donar resposta al 5é objectiu de la recerca, observant que, les propietats relatives definides com la resistència a tracció en relació al rendiment eren millors en les fibres MP, seguides per les TMP i les CTMP. Aquest indici de propietats mecàniques en certa manera ajuden a començar a provar el 4t objectiu de la tesi, ja que els materials compostos mostren propietats mecàniques semblants a altres materials comercials, reforçats amb fibres de vidre. Les fibres de fusta de taronger són competitives com a reforç, donant resistències a tracció equivalents a les del polipropilè reforçat amb un 20% de fibra de vidre, quan les primeres s'afegeixen en una quantitat del 50%. De totes maneres, encara que alguns tractaments oferien millors propietats, els lleugers increments de la resistència a la tracció no justifiquen l'ús dels processos CTMP amb OPF, degut al seu menor rendiment respecta a la biomassa inicial, així, les propietats relatives definides com la resistència a tracció en relació al rendiment són millors en les fibres MP, seguides per les TMP i les CTMP. Una anàlisi de l'estructura de la matriu va establir que l'augment del percentatge de fibres en el compòsit augmenta el grau de cristal·linitat de la matriu, fet que afecta positivament la rigidesa dels materials.

Les dades de resistència a tracció varen mostrar que els materials eren potencialment interesants per al seu ús industrial, de totes maneres, calia verificar la seva rigidesa. En el 3r article de la sèrie es va analitzar i modelar la micromecànica dels mòduls de Young dels materials. Una vegada fets els modelats i les proves de laboratori, es va reforçar l'objectiu 4t, ja que els valors de rigidització també s'acostaven als de materials presents al mercat. Es va concloure que les fibres de poda de taronger donen valors del mòdul de Young que permeten el seu ús per a reforçar materials amb funció semiestructural. Es va usar la regla de les mescles per modelar el comportament del mòdul de Young, donant resposta a l'objectiu 6é.

Una vegada establertes les propietats mecàniques estàtiques es va veure interesant avaluar les propietats tèrmiques, ja que les temperatures de processament podia reduir les propietats de les fibres o fins i tot generar emissions volàtils. L'objectiu 7é de la recerca està relacionat amb el

coneixement de les temperatures de fusió i de degradació dels materials. Una vegada fetes les proves, es va comprovar que els materials reforçats amb fibres lignocelulósiques de poda taronger exhibien dos passos degradatius, que corresponen a les diferents característiques del polipropilè i la fibra. Al mateix temps, també es va observar que l'expansió tèrmica dels materials compostos disminuïa a mesura que la quantitat de reforç augmenta. Aquest resultat s'explica per el menor coeficient d'expansió del reforç en comparació amb la de la matriu.

Finalment, per complir l'objectiu 8é i afinaçar el 4t, es va investigar, en el 5é article, el possible ús dels materials compostos com a barrera sonora, i la seva possible utilització en les construccions, com una alternativa als panells de cartró guix. Una vegada analitzats i modelats els paràmetres d'aïllament sonor es va comprovar que el polipropilè reforçat amb fibres de poda de taronger oferia una solució alternativa al panell de cartró guix que és la solució actualment més utilitzada, a més a més el nou compòsit ofereix nivells d'aïllament sonor superiors.

A la fi, la recerca ha donat resposta a tots els objectius plantejats, mitjançant una sèrie d'articles que han encadenat els resultats i han obert la porta al seu ús en altres elements constructius.

9 FUTURES LÍNIES DE RECERCA

Les futures línies de recerca que neixen de la present tesi doctoral son:

- Estudi de les propietats d'aïllament tèrmic dels materials compostos estudiats
- Comportament a esforços dinàmics dels materials
- Aplicació dels materials a la construcció. Anàlisi de viabilitat del seu ús per fabricar materials de construcció.

Anàlisi del cicle de vida de productes de a construcció fabricats amb els materials compostos estudiats.

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CAPÍTOL V

BIBLIOGRAFIA

10 BIBLIOGRAFIA

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