



HAL
open science

Orange Wood Fiber Reinforced Polypropylene Composites: Thermal Properties

Rafel Reixach, Josep Puig, José Alberto Méndez, Jordi Girones, Francesc X.
Espinach, Gérard Arbat, Pere Mutjé

► **To cite this version:**

Rafel Reixach, Josep Puig, José Alberto Méndez, Jordi Girones, Francesc X. Espinach, et al.. Orange Wood Fiber Reinforced Polypropylene Composites: Thermal Properties. *Bioresources*, 2015, 10 (2), pp.2156-2166. 10.15376/biores.10.2.2156-2166 . hal-01257420

HAL Id: hal-01257420

<https://hal-mines-paristech.archives-ouvertes.fr/hal-01257420>

Submitted on 18 Jan 2016

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

Orange Wood Fiber Reinforced Polypropylene Composites: Thermal Properties

Rafel Reixach,^a Josep Puig,^b José Alberto Méndez,^b Jordi Gironès,^c
Francesc X. Espinach,^d Gerard Arbat,^{e,*} and Pere Mutjé^b

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

*Contact information: a: Department of Architecture and Construction Engineering, University of Girona, C/ Ma Aurèlia Capmany, 61, 17071 Girona, Spain; b: Grup Lepamap, Departament d'Enginyeria Química Agrària i Tecnologia Agroalimentària, Universitat de Girona, C/ Ma Aurèlia Capmany, 61, 17071 Girona, Spain; c: Mines Paristech, Centre de Mise en Forme des Matériaux (CEMEF), UMR CNRS 7635, BP 207, 06904 – Sophia Antipolis CEDEX, France; d: Design, Development and Product Innovation. Dept. of Organization Business, University of Girona, C/ Ma Aurèlia Capmany, 61, 17071 Girona, Spain; e: Department of Chemical and Agricultural Engineering and Agrifood Technology, University of Girona, C/ Ma Aurèlia Capmany, 61, 17071 Girona, Spain; *Corresponding author: gerard.arbat@udg.edu*

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 CO₂ 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/m³. 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/cm², 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 N₂). 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 N₂).

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 N₂).

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).

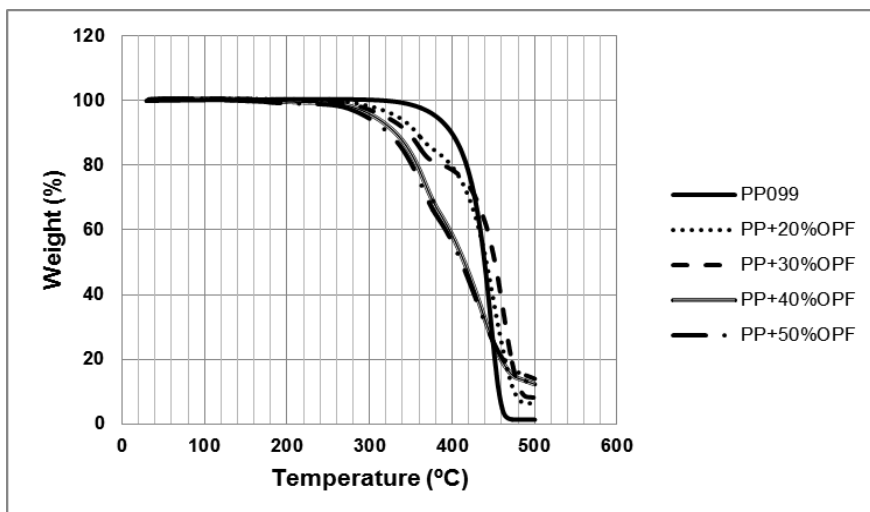


Fig. 1. TGA of 20 to 50 wt.% OPF reinforced PP composite materials

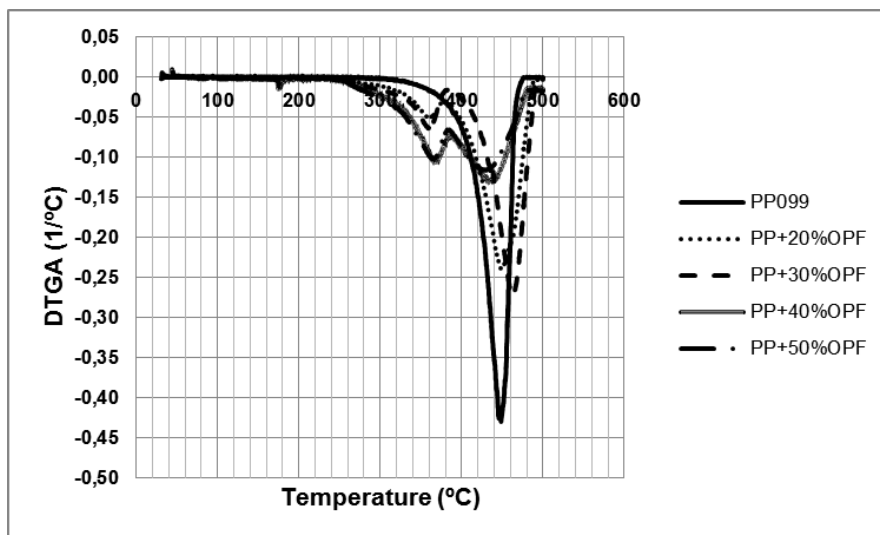


Fig. 2. DTGA of 20 to 50 wt.% OPF-reinforced PP composite materials

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

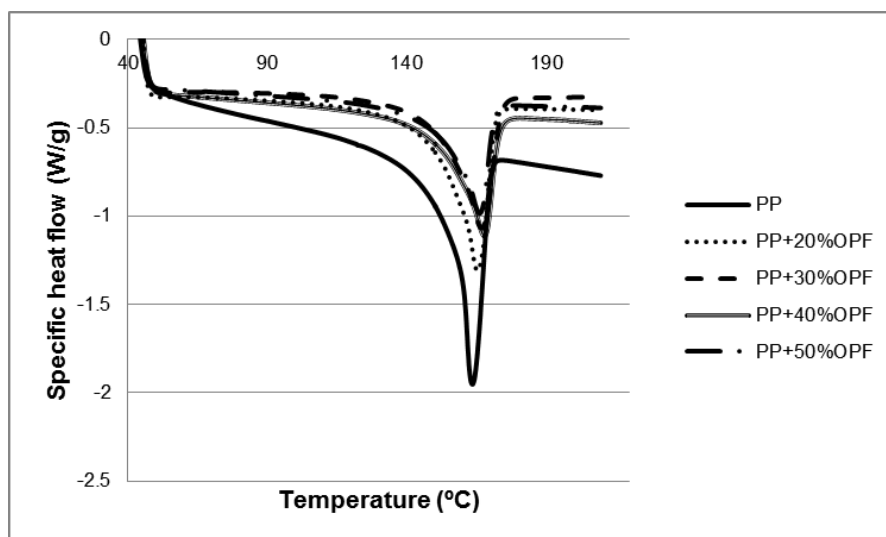
Differential Scanning Calorimetry (DSC)

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

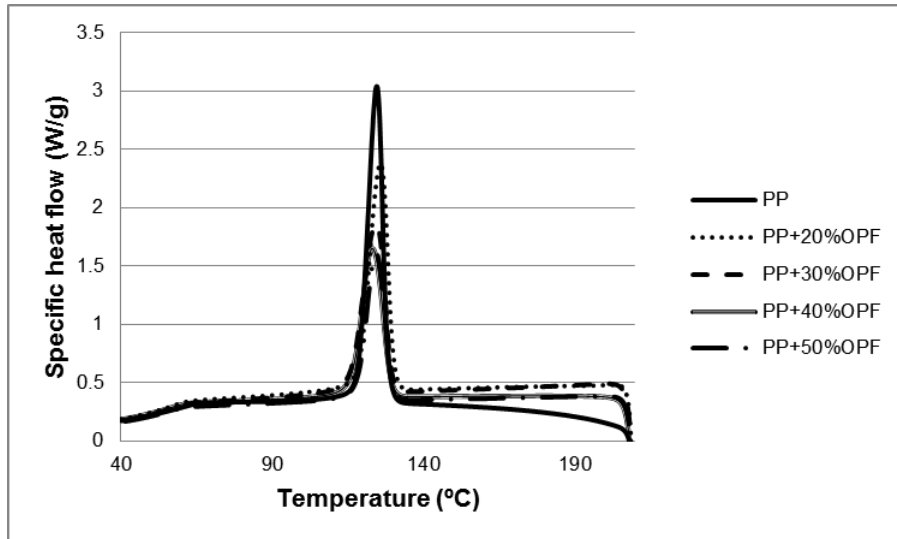


Fig. 4. Graphical comparison of the crystallization exotherm of the matrix and the fiber-reinforced orange wood

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.

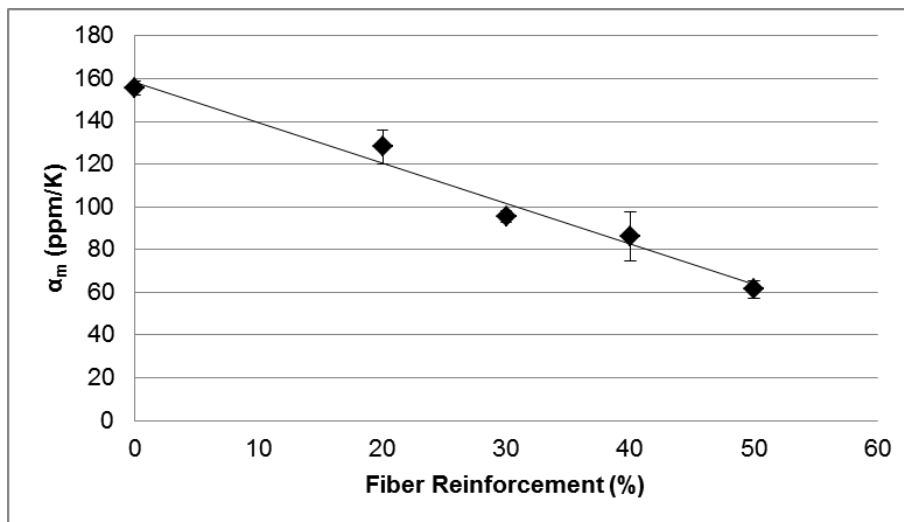


Fig. 5. Coefficient of thermal expansion as a function of fiber content

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 $155 \mu\text{m}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$ for neat PP to $61 \mu\text{m}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$ 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.

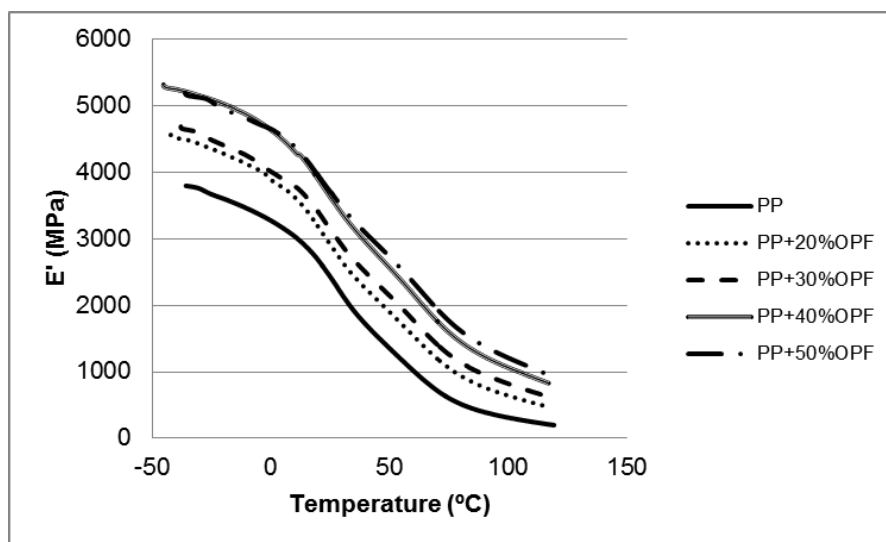


Fig. 6. Storage modulus of PP and PP composites reinforced with orange fiber

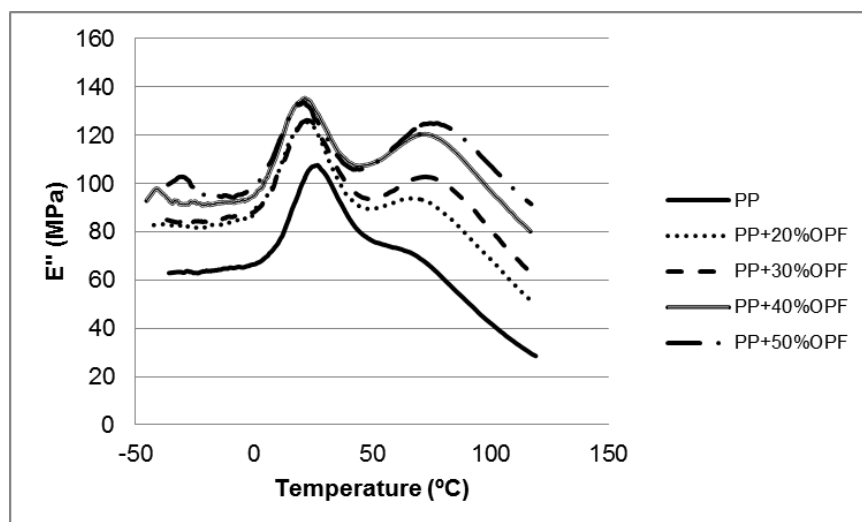


Fig. 7. Loss modulus of PP and PP composites reinforced with orange fiber

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 _{peak2}
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.

ACKNOWLEDGMENTS

The authors are grateful for the support of the EMCI - *Ministerio de Ciencia e Innovación* (MICINN) for funding the research by the specific Research Program CTQ2010-21660-C03-03.

REFERENCES CITED

- Amash, A., and Zugenmaier, P. (1998). "Study on cellulose and xylan filled polypropylene composites," *Polymer Bulletin* 40(2-3), 251-258. DOI: 10.1007/s002890050249
- Amash, A., and Zugenmaier, P. (2000). "Morphology and properties of isotropic and oriented samples of cellulose fibre–polypropylene composites," *Polymer* 41(4), 1589-1596. DOI: 10.1016/S0032-3861(99)00273-6
- Ashori, A., and Nourbakhsh, A. (2009). "Mechanical Behavior of agro-residue-reinforced polypropylene composites," *J. Appl. Polym. Sci.* 111(5), 2616-2620. DOI: 10.1002/app.29345
- Bigg, D., Hiscock, D., Preston, J., and Bradbury, E. (1988). "High performance thermoplastic matrix composites," *J. Thermoplastic Compos. Mater.* 1(2), 146-160. DOI: 10.1177/089270578800100203
- Dittenber, D. B., and GangaRao, H. V. (2012). "Critical review of recent publications on use of natural composites in infrastructure," *Composites Part A: Applied Science and Manufacturing* 43(8), 1419-1429. DOI: 10.1016/j.compositesa.2011.11.019
- Espigulé, E., Puigvert, X., Vilaseca, F., Mendez, J. A., Mutjé, P., and Girones, J. (2013). "Thermoplastic starch-based composites reinforced with rape fibers: Water uptake and thermomechanical properties," *BioResources* 8(2), 2620-2630. DOI: 10.15376/biores.8.2.2620-2630
- Fernández-Puratich, H., Oliver-Villanueva, J. V., Alfonso-Solar, D., and Penalvo-Lopez, E. (2013). "Quantification of potential lignocellulosic biomass in fruit trees grown in mediterranean regions," *BioResources* 8(1), 88-103.
- Gwon, J. G., Lee, S. Y., and Kim, J. H. (2014). "Thermal degradation behavior of polypropylene base wood plastic composites hybridized with metal (aluminum, magnesium) hydroxides," *J. Appl. Polym. Sci.* 131(7), 40120-40120. DOI: 10.1002/app.40120
- Julian, F., Espinach, F., Verdaguer, N., Pelach, M., and Vilaseca, F. (2012a). "Design and development of fully biodegradable products from starch biopolymer and corn stalk fibres," *Journal of Biobased Materials and Bioenergy* 6(4), 410-417. DOI: 10.1166/jbmb.2012.1228
- Julian, F., Méndez, J. A., Espinach, F. X., Verdaguer, N., Mutje, P., and Vilaseca, F. (2012b). "Bio-based composites from stone groundwood applied to new product development," *BioResources* 7(4), 5829-5942. DOI: 10.15376/biores.7.4.5829-5842
- Kim, B. J., Yao, F., Han, G., Wang, Q., and Wu, Q. (2013). "Mechanical and physical properties of core-shell structured wood plastic composites: Effect of shells with hybrid mineral and wood fillers," *Composites Part B: Engineering* 45(1), 1040-1048. DOI: 10.1016/j.compositesb.2012.07.031
- Ku, H., Wang, H., Pattarachaiyakoop, N., and Trada, M. (2011). "A review on the tensile properties of natural fiber reinforced polymer composites," *Composites Part B: Engineering* 42(4), 856-873. DOI: 10.1016/j.compositesb.2011.01.010
- Kumar, V., Tyagi, L., and Sinha, S. (2011). "Wood flour–reinforced plastic composites: A review," *Reviews in Chemical Engineering* 27(5-6), 253-264. DOI: 10.1515/REVCE.2011.006

- Liu, T., Wang, Q., Xie, Y., Lee, S., and Wu, Q. (2014). "Effects of use of coupling agents on the properties of microfibrillar composite based on high-density polyethylene and polyamide-6," *Polymer Bulletin* 71(3), 685-703. DOI: 10.1007/s00289-013-1086-x
- López, J. P., Gironès, J., Méndez, J. A., El Mansouri, N.-E., Llop, M., Mutjé, P., and Vilaseca, F. (2012a). "Stone-ground wood pulp-reinforced polypropylene composites: Water uptake and thermal properties," *BioResources* 7(4), 5478-5487.
- López, J. P., Méndez, J. A., Espinach, F. X., Julián, F., Mutjé, P., and Vilaseca, F. (2012b). "Tensile strength characteristics of polypropylene composites reinforced with stone groundwood fibers from softwood," *BioResources* 7(3), 5478-5487.
- López, J. P., Mutje, P., Carvalho, A. J. F., Curvelo, A. A. S., and Girones, J. (2013). "Newspaper fiber-reinforced thermoplastic starch biocomposites obtained by melt processing: Evaluation of the mechanical, thermal and water sorption properties," *Industrial Crops and Products* 44, 300-305. 10.1016/j.indcrop.2012.11.020
- Lu, J. Z., Wu, Q., and McNabb, H. S. (2000). "Chemical coupling in wood fiber and polymer composites: a review of coupling agents and treatments," *Wood and Fiber Science* 32(1), 88-104.
- Maldas, D., and Kokta, B. (1989). "Improving adhesion of wood fiber with polystyrene by the chemical treatment of fiber with a coupling agent and the influence on the mechanical properties of composites," *Journal of Adhesion Science and Technology* 3(1), 529-539 . DOI: 10.1163/156856189X00380
- Mishra, S., and Sain, M. (2009). "Commercialization of wheat straw as reinforcing filler for commodity thermoplastics," *Journal of Natural Fibers* 6(1), 83-97. DOI: 10.1080/15440470802703851
- Neagu, R. C., and Gamstedt, E. K. (2007). "Modelling of effects of ultrastructural morphology on the hygroelastic properties of wood fibres," *Journal of Materials Science* 42(24), 10254-10274. DOI: 0.1007/s10853-006-1199-9
- Quan, H., Li, Z.-M., Yang, M.-B., and Huang, R. (2005). "On transcrystallinity in semi-crystalline polymer composites," *Composites Science and Technology* 65(7), 999-1021. DOI: 10.1016/j.compscitech.2004.11.015
- Reixach, R., Espinach, F. X., Franco-Marques, E., Ramirez de Cartagena, F., Pellicer, N., Tresserras, J., and Mutje, P. (2013a). "Modeling of the Tensile moduli of mechanical, thermomechanical, and chemi-thermomechanical pulps from orange tree pruning," *Polymer Composites* 34(11), 1840-1846. DOI: 10.1002/pc.22589
- Reixach, R., Franco-Marques, E., El Mansouri, N.-E., Ramirez de Cartagena, F., Arbat, G., Espinach, F. X., and Mutje, P. (2013b). "Micromechanics of mechanical, thermomechanical, and chemi-thermomechanical pulp from orange tree pruning as polypropylene reinforcement: A comparative study," *BioResources* 8(3), 3231-3246. DOI: 10.15376/biores.8.3.3231-3246
- Rosa, S. M., Nachtigall, S. M., and Ferreira, C. A. (2009). "Thermal and dynamic-mechanical characterization of rice-husk filled polypropylene composites," *Macromolecular Research* 17(1), 8-13. DOI: 10.1007/BF03218594
- Rukmini, K., Ramaraj, B., Shetty, S. K., Taraiya, A., Bandyopadhyay, S., and Siddaramaiah. (2013). "Development of eco-friendly cotton fabric reinforced polypropylene composites: Mechanical, thermal, and morphological properties," *Advances in Polymer Technology* 32(1), 8-13. DOI: 10.1007/BF03218594
- Sarlin, J., and Immonen, K. (2013). "Poly (propylene) composite with hybrid nanofiller: Dynamic properties," *J. Appl. Polym. Sci.* 128(6), 3734-3742. DOI: 10.1002/adv.21327

Thamae, T., Marien, R., Chong, L., Wu, C., and Baillie, C. (2008). "Developing and characterizing new materials based on waste plastic and agro-fibre," *J. Mater. Sci.* 43(12), 4057-4068. DOI: 10.1007/s10853-008-2495-3

Article submitted: November 10, 2014; Peer review completed: January 29, 2015;
Revised version received and accepted: February 6, 2015; Published: February 12, 2015.