YOUR PROOFS (13125) FROM Journal of Applied Polymer Science ARE AVAILABLE FOR CORRECTIONS
=====
Journal of Applied Polymer Science Published by John Wiley & Sons, Inc.

Dear Author,

YOUR PAGE PROOFS ARE AVAILABLE IN PDF FORMAT; please refer to this URL address http://rapidproof.cadmus.com/RapidProof/retrieval/index.jsp

Login: your e-mail address
Password: ----

The site contains 1 file. You will need to have Adobe Acrobat Reader software to read these files. This is free software and is available for user downloading at http://www.adobe.com/products/acrobat/readstep.html. If you have the Notes annotation tool (not contained within Acrobat reader), you can make corrections electronically and return them to Wiley as an e-mail attachment (see the Notes tool instruction sheet). Alternatively, if you would prefer to receive a paper proof by regular mail, please contact Teressa Beard (e-mail: beardt@cadmus.com; phone: 800-238-3814 x602 or 717-721-2602). Be sure to include your article number.

This file contains:

Author Instructions Checklist
Adobe Acrobat Users - NOTES tool sheet
Reprint Order form
A copy of your page proofs for your article

After printing the PDF file, please read the page proofs carefully and:

1) indicate changes or corrections in the margin of the page proofs;
2) answer all queries (footnotes A,B,C, etc.) on the last page of the PDF proof;
3) proofread any tables and equations carefully;
4) check that any Greek, especially "mu", has translated correctly.

Special Notes:

Please return hard copy corrections and reprint order form to Wiley via express/overnight service or fax as soon as possible (to Sheila Kaminsky; see address and numbers below). If you fax your corrections, please include a cover page detailing the corrections as changes may be distorted during transmission. If you have access to Adobe Acrobat 4.0, annotated PDF files may be returned via e-mail.

Your article will be published online via our EarlyView service after correction receipt. Your prompt attention to and return of page proofs is crucial to faster publication of your work. Thank you for your cooperation.

Return to:

Sheila Kaminsky
John Wiley & Sons, Inc.
111 River Street

Hoboken, NJ 07030
U.S.A.
(See fax number and e-mail address below.)

If you experience technical problems, please contact Teressa Beard (e-mail: beardt@cadmus.com, phone: 800-238-3814 (x602)or 717-721-2602).

If you have any questions regarding your article, please contact me. PLEASE ALWAYS INCLUDE YOUR ARTICLE NO. (13125) WITH ALL CORRESPONDENCE.

This e-proof is to be used only for the purpose of returning corrections to the publisher.

Sincerely,

Sheila Kaminsky
Senior Production Editor
John Wiley & Sons, Inc.
E-mail: sheila.kaminsky@wiley.com
Tel: 201-748-6540
Fax: 201-748-6052

WILEY
Publishers Since 1807

111 RIVER STREET, HOBOKEN, NJ 07030

*****IMMEDIATE RESPONSE REQUIRED*****
Please follow these instructions to avoid delay of publication.

☐ **READ PROOFS CAREFULLY**
- This will be your only chance to review these proofs.
- Please note that the volume and page numbers shown on the proofs are for position only.

☐ **ANSWER ALL QUERIES ON PROOFS** (Queries for you to answer are attached as the last page of your proof.)
- Mark all corrections directly on the proofs. Note that excessive author alterations may ultimately result in delay of publication and extra costs may be charged to you.

☐ **CHECK FIGURES AND TABLES CAREFULLY** (Color figures will be sent under separate cover.)
- Check size, numbering, and orientation of figures.
- All images in the PDF are downsampled (reduced to lower resolution and file size) to facilitate Internet delivery. These images will appear at higher resolution and sharpness in the printed article.
- Review figure legends to ensure that they are complete.
- Check all tables. Review layout, title, and footnotes.

☐ **COMPLETE REPRINT ORDER FORM**
- Fill out the attached reprint order form. It is important to return the form even if you are not ordering reprints. You may, if you wish, pay for the reprints with a credit card. Reprints will be mailed only after your article appears in print. This is the most opportune time to order reprints. If you wait until after your article comes off press, the reprints will be considerably more expensive.

RETURN ☐**PROOFS**
☐**REPRINT ORDER FORM**
☐**CTA (If you have not already signed one)**

RETURN WITHIN 48 HOURS OF RECEIPT VIA FAX TO 201-748-6052

QUESTIONS?
Sheila Kaminsky, Senior Production Editor
Phone: 201-748-6540
E-mail: sheila.kaminsky@wiley.com
Refer to journal acronym and article production number

Softproofing for advanced Adobe Acrobat Users - NOTES tool

NOTE: ACROBAT READER FROM THE INTERNET DOES NOT CONTAIN THE NOTES TOOL USED IN THIS PROCEDURE.

Acrobat annotation tools can be very useful for indicating changes to the PDF proof of your article. By using Acrobat annotation tools, a full digital pathway can be maintained for your page proofs.

The NOTES annotation tool can be used with either Adobe Acrobat 3.0x or Adobe Acrobat 4.0. Other annotation tools are also available in Acrobat 4.0, but this instruction sheet will concentrate on how to use the NOTES tool. Acrobat Reader, the free Internet download software from Adobe, DOES NOT contain the NOTES tool. In order to softproof using the NOTES tool you must have the full software suite Adobe Acrobat Exchange 3.0x or Adobe Acrobat 4.0 installed on your computer.

Steps for Softproofing using Adobe Acrobat NOTES tool:

1. Open the PDF page proof of your article using either Adobe Acrobat Exchange 3.0x or Adobe Acrobat 4.0. Proof your article on-screen or print a copy for markup of changes.

2. Go to File/Preferences/Annotations (in Acrobat 4.0) or File/Preferences/Notes (in Acrobat 3.0) and enter your name into the “default user” or “author” field. Also, set the font size at 9 or 10 point.

3. When you have decided on the corrections to your article, select the NOTES tool from the Acrobat toolbox and click in the margin next to the text to be changed.

4. Enter your corrections into the NOTES text box window. Be sure to clearly indicate where the correction is to be placed and what text it will effect. If necessary to avoid confusion, you can use your TEXT SELECTION tool to copy the text to be corrected and paste it into the NOTES text box window. At this point, you can type the corrections directly into the NOTES text box window. **DO NOT correct the text by typing directly on the PDF page.**

5. Go through your entire article using the NOTES tool as described in Step 4.

6. When you have completed the corrections to your article, go to File/Export/Annotations (in Acrobat 4.0) or File/Export/Notes (in Acrobat 3.0). Save your NOTES file to a place on your harddrive where you can easily locate it. **Name your NOTES file with the article number assigned to your article in the original softproofing e-mail message.**

7. **When closing your article PDF be sure NOT to save changes to original file.**

8. To make changes to a NOTES file you have exported, simply re-open the original PDF proof file, go to File/Import/Notes and import the NOTES file you saved. Make changes and re-export NOTES file keeping the same file name.

9. When complete, attach your NOTES file to a reply e-mail message. Be sure to include your name, the date, and the title of the journal your article will be printed in.

John Wiley & Sons, Inc.
Publishers Since 1807

REPRINT BILLING DEPARTMENT • 111 RIVER STREET • HOBOKEN, NJ 07030
PHONE: (201) 748-8789; FAX: (201) 748-6326
E-MAIL: reprints @ wiley.com

PREPUBLICATION REPRINT ORDER FORM

Please complete this form even if you are not ordering reprints. This form **MUST** be returned with your corrected proofs and original manuscript. Your reprints will be shipped approximately 4 weeks after publication. Reprints ordered after printing are substantially more expensive.

JOURNAL: *JOURNAL OF APPLIED POLYMER SCIENCE* _____ VOLUME_____ ISSUE_____

TITLE OF MANUSCRIPT____

MS. NO.____________ NO. OF PAGES______ AUTHOR(S)______________________________

REPRINTS 8 1/4 X 11

No. of Pages	100 Reprints	200 Reprints	300 Reprints	400 Reprints	500 Reprints
	$	$	$	$	$
1-4	336	501	694	890	1,052
5-8	469	703	987	1,251	1,477
9-12	594	923	1,234	1,565	1,850
13-16	714	1,156	1,527	1,901	2,273
17-20	794	1,340	1,775	2,212	2,648
21-24	911	1,529	2,031	2,536	3,037
25-28	1,004	1,707	2,267	2,828	3,388
29-32	1,108	1,894	2,515	3,135	3,755
33-36	1,219	2,092	2,773	3,456	4,143
37-40	1,329	2,290	3,033	3,776	4,528

** REPRINTS ARE ONLY AVAILABLE IN LOTS OF 100. IF YOU WISH TO ORDER MORE THAN 500 REPRINTS, PLEASE CONTACT OUR REPRINTS DEPARTMENT AT (201)748-8789 FOR A PRICE QUOTE.

COVERS

100 Covers - $90	200 Covers - $145	300 Covers - $200
400 Covers - $255	500 Covers - $325	Additional 100s - $65

☐ Please send me __________ reprints of the above article at......................	$____________
☐ Please send me __________ Generic covers of the above journal at......................	$____________
Please add appropriate State and Local Tax {Tax Exempt No.__________________}	$____________
Please add 5% Postage and Handling..	$____________
TOTAL AMOUNT OF ORDER**	$____________

***International orders must be paid in U.S. currency and drawn on a U.S. bank*

Please check one: ☐ Check enclosed ☐ Bill me ☐ Credit Card
If credit card order, charge to: ☐ American Express ☐ Visa ☐ MasterCard ☐ Discover
Credit Card No.____________________________ Signature____________________________ Exp. Date___________

Bill To:	**Ship To:**
Name________________________________	Name________________________________
Address/Institution____________________	Address/Institution____________________
____________________________________	____________________________________
____________________________________	____________________________________
____________________________________	____________________________________

Purchase Order No. ____________________________ Phone ________________ Fax ________________
E-mail: ________________________________

WILEY
Publishers Since 1807

111 River Street
Hoboken, NJ 07030
201.748.6000
FAX 201.748.6052

COPYRIGHT TRANSFER AGREEMENT

Date:

To:

Production/Contribution
ID# _______________
Publisher/Editorial office use only

Re: Manuscript entitled____
____(the "Contribution")
for publication in ____(the "Journal")
published by Wiley Periodicals, Inc. ("Wiley").

Dear Contributor(s):

Thank you for submitting your Contribution for publication. In order to expedite the editing and publishing process and enable Wiley to disseminate your work to the fullest extent, we need to have this Copyright Transfer Agreement signed and returned to us as soon as possible. If the Contribution is not accepted for publication this Agreement shall be null and void.

A. COPYRIGHT

1. The Contributor assigns to Wiley, during the full term of copyright and any extensions or renewals of that term, all copyright in and to the Contribution, including but not limited to the right to publish, republish, transmit, sell, distribute and otherwise use the Contribution and the material contained therein in electronic and print editions of the Journal and in derivative works throughout the world, in all languages and in all media of expression now known or later developed, and to license or permit others to do so.

2. Reproduction, posting, transmission or other distribution or use of the Contribution or any material contained therein, in any medium as permitted hereunder, requires a citation to the Journal and an appropriate credit to Wiley as Publisher, suitable in form and content as follows: (Title of Article, Author, Journal Title and Volume/Issue Copyright © [year] Wiley Periodicals, Inc. or copyright owner as specified in the Journal.)

B. RETAINED RIGHTS

Notwithstanding the above, the Contributor or, if applicable, the Contributor's Employer, retains all proprietary rights other than copyright, such as patent rights, in any process, procedure or article of manufacture described in the Contribution, and the right to make oral presentations of material from the Contribution.

C. OTHER RIGHTS OF CONTRIBUTOR

Wiley grants back to the Contributor the following:

1. The right to share with colleagues print or electronic "preprints" of the unpublished Contribution, in form and content as accepted by Wiley for publication in the Journal. Such preprints may be posted as electronic files on the Contributor's own website for personal or professional use, or on the Contributor's internal university or corporate networks/intranet, or secure external website at the Contributor's institution, but not for commercial sale or for any systematic external distribution by a third party (e.g., a listserve or database connected to a public access server). Prior to publication, the Contributor must include the following notice on the preprint: "This is a preprint of an article accepted for publication in [Journal title] © copyright (year) (copyright owner as specified in the Journal)". After publication of the Contribution by Wiley, the preprint notice should be amended to read as follows: "This is a preprint of an article published in [include the complete citation information for the final version of the Contribution as published in the print edition of the Journal]", and should provide an electronic link to the Journal's WWW site, located at the following Wiley URL: http://www.interscience.Wiley.com/. The Contributor agrees not to update the preprint or replace it with the published version of the Contribution.

2. The right, without charge, to photocopy or to transmit online or to download, print out and distribute to a colleague a copy of the published Contribution in whole or in part, for the colleague's personal or professional use, for the

advancement of scholarly or scientific research or study, or for corporate informational purposes in accordance with Paragraph D.2 below.

3. The right to republish, without charge, in print format, all or part of the material from the published Contribution in a book written or edited by the Contributor.

4. The right to use selected figures and tables, and selected text (up to 250 words, exclusive of the abstract) from the Contribution, for the Contributor's own teaching purposes, or for incorporation within another work by the Contributor that is made part of an edited work published (in print or electronic format) by a third party, or for presentation in electronic format on an internal computer network or external website of the Contributor or the Contributor's employer.

5. The right to include the Contribution in a compilation for classroom use (course packs) to be distributed to students at the Contributor's institution free of charge or to be stored in electronic format in datarooms for access by students at the Contributor's institution as part of their course work (sometimes called "electronic reserve rooms") and for in-house training programs at the Contributor's employer.

D. CONTRIBUTIONS OWNED BY EMPLOYER

1. If the Contribution was written by the Contributor in the course of the Contributor's employment (as a "work-made-for-hire" in the course of employment), the Contribution is owned by the company/employer which must sign this Agreement (in addition to the Contributor's signature), in the space provided below. In such case, the company/employer hereby assigns to Wiley, during the full term of copyright, all copyright in and to the Contribution for the full term of copyright throughout the world as specified in paragraph A above.

2. In addition to the rights specified as retained in paragraph B above and the rights granted back to the Contributor pursuant to paragraph C above, Wiley hereby grants back, without charge, to such company/employer, its subsidiaries and divisions, the right to make copies of and distribute the published Contribution internally in print format or electronically on the Company's internal network. Upon payment of Wiley's reprint fee, the institution may distribute (but not resell) print copies of the published Contribution externally. Although copies so made shall not be available for individual re-sale, they may be included by the company/employer as part of an information package included with software or other products offered for sale or license. Posting of the published Contribution by the institution on a public access website may only be done with Wiley's written permission, and payment of any applicable fee(s).

E. GOVERNMENT CONTRACTS

In the case of a Contribution prepared under U.S. Government contract or grant, the U.S. Government may reproduce, without charge, all or portions of the Contribution and may authorize others to do so, for official U.S. Government purposes only, if the U.S. Government contract or grant so requires. (U.S. Government Employees: see note at end.)

F. COPYRIGHT NOTICE

The Contributor and the company/employer agree that any and all copies of the Contribution or any part thereof distributed or posted by them in print or electronic format as permitted herein will include the notice of copyright as stipulated in the Journal and a full citation to the Journal as published by Wiley.

G. CONTRIBUTOR'S REPRESENTATIONS

The Contributor represents that the Contribution is the Contributor's original work. If the Contribution was prepared jointly, the Contributor agrees to inform the co-Contributors of the terms of this Agreement and to obtain their signature to this Agreement or their written permission to sign on their behalf. The Contribution is submitted only to this Journal and has not been published before, except for "preprints" as permitted above. (If excerpts from copyrighted works owned by third parties are included, the Contributor will obtain written permission from the copyright owners for all uses as set forth in Wiley's permissions form or in the Journal's Instructions for Contributors, and show credit to the sources in the Contribution.) The Contributor also warrants that the Contribution contains no libelous or unlawful statements, does not infringe upon the rights (including without limitation the copyright, patent or trademark rights) or the privacy of others, or contain material or instructions that might cause harm or injury.

CHECK ONE:

[____] Contributor-owned work

Contributor's signature ____________________ Date ________

Type or print name and title ____________________

Co-contributor's signature ____________________ Date ________

Type or print name and title ____________________

ATTACHED ADDITIONAL SIGNATURE PAGE AS NECESSARY

[____] Company/Institution-owned work
(made-for-hire in the
course of employment)

Company or Institution (Employer-for-Hire) ____________________ Date ________

Authorized signature of Employer ____________________ Date ________

[____] U.S. Government work

Note to U.S. Government Employees

A contribution prepared by a U.S. federal government employee as part of the employee's official duties, or which is an official U.S. Government publication is called a "U.S. Government work," and is in the public domain in the United States. In such case, the employee may cross out Paragraph A.1 but must sign and return this Agreement. If the Contribution was not prepared as part of the employee's duties or is not an official U.S. Government publication, it is not a U.S. Government work.

[____] U.K. Government work (Crown Copyright)

Note to U.K. Government Employees

The rights in a Contribution prepared by an employee of a U.K. government department, agency or other Crown body as part of his/her official duties, or which is an official government publication, belong to the Crown. In such case, Wiley will forward the relevant form to the Employee for signature.

WILEY
Publishers Since 1807

111 RIVER STREET, HOBOKEN, NJ 07030

Telephone Number: Facsimile Number:

To: Sheila Kaminsky

Company:

Phone: 201-748-6540

Fax: 201-748-6052

From:

Date:

Pages including this cover page:

Message:

Re:

Thermal and Mechanical Properties of Woodflour/Tannin Adhesive Composites

M. Mosiewicki, M. I. Aranguren, J. Borrajo

Institute of Materials Science and Technology (INTEMA), University of Mar del Plata–National Research Council (CONICET), Av. Juan B. Justo 4302, (7600) Mar del Plata, Argentina

Received 4 April 2003; accepted 22 August 2003
Published online 00 Month 2004 in Wiley InterScience (www.interscience.wiley.com). DOI 10.1002/app.13498

ABSTRACT: Composite materials formulated with a natural polyphenolic matrix (commercial tannin adhesive made from quebracho tannin extract), pine woodflour as reinforcing material, and hexamethylenetetramine as hardener were prepared and tested. Scanning electron microscopy of fractured samples was used to analyze the efficiency of the wetting and adhesion of the filler to the surrounding matrix. Thermogravimetric analysis was used in the thermal characterization of the woodflour and the tannin extract. Flexural, compression, and dynamic-mechanical tests were performed on composites to study the relationship of the filler content and particle size with the composite final properties. Moreover, the influence of the moisture content on the physical and mechanical properties of the different composites was analyzed. Results indicated that the mechanical properties were severely affected by the absorbed moisture. © 2004 Wiley Periodicals, Inc. J Appl Polym Sci 91: 000–000, 2004

Key words: tannin adhesives; woodflour composites; microstructure; thermal properties; mechanical properties

Author Proof

INTRODUCTION

In many countries, the development of new adhesives is driven by environmental considerations, which include the reduction of emissions of volatile organic compounds, such as phenol and formaldehyde. Most scientific studies and technological reports on the applications of tannin extracts are related to their use in the manufacture of adhesives for particleboards and plywood, as well as for laminated woods. On the other hand the use of woodflour as a reinforcing filler is an attractive commercial alternative because of its low cost and wide availability.

Polyflavonoid tannin extracts have been produced and used industrially in many applications since the end of the nineteenth century.[1] Among these uses, the major applications have been as tanning agents for the manufacture of leather and wood adhesives.[1,2] Polyflavonoid tannins are natural polyphenolic materials, F1 composed mostly of flavan-3ol repeating units (Fig. 1) and smaller fractions of polysaccharides and sugars. These polyphenolic materials can be hardened by reaction with formaldehyde or hexamethylenetetramine (HEXA) crosslinking agents.[1,2]

The reaction of HEXA with tannin adhesives in aqueous solutions was studied by Pizzi,[3,4] who showed that HEXA is not a formaldehyde-yielding hardener and thus it leads to cured products with low formaldehyde emissions. The crosslinking reactions proceed by formation of reactive HEXA fragments or intermediates that react with the phenolic nuclei of the polyflavonoid tannins.

The most widely used industrial tannins are obtained from the wood of the quebracho tree (*Schinopsis balansae*, Argentine) and from the bark of mimosa (*Acacia mearnsii*, Brazil and South Africa). Most scientific studies and technological reports on the application of tannin extracts are related to their use in the manufacture of adhesives for particleboards and plywood, as well as for laminated woods.[1,2] Studies that report the behavior of these adhesives for the manufacture of molding powders or fiber composite materials are scarce in the open literature.[5]

Many authors have studied and reported information about the characterization of different tannin extracts and their reactions with several hardeners.[1,2,5–8] Nevertheless, analyses of the thermal and mechanical properties of these composite materials have not yet been published.

The focus of this work was on the analysis of the thermal and mechanical properties of composite materials formulated from a commercial quebracho tannin adhesive, pine woodflour, and HEXA as hardener: the effect of moisture on the final properties of these materials is also addressed.

Water absorption, flexural, compression, and dynamic-mechanical tests were performed on the composites and the relationship between the filler (concentration and particle size) and the measured properties was studied.

Correspondence to: M. Mosiewicki (mirna@fi.mdp.edu.ar).

Journal of Applied Polymer Science, Vol. 91, 000–000 (2004)
© 2004 Wiley Periodicals, Inc.

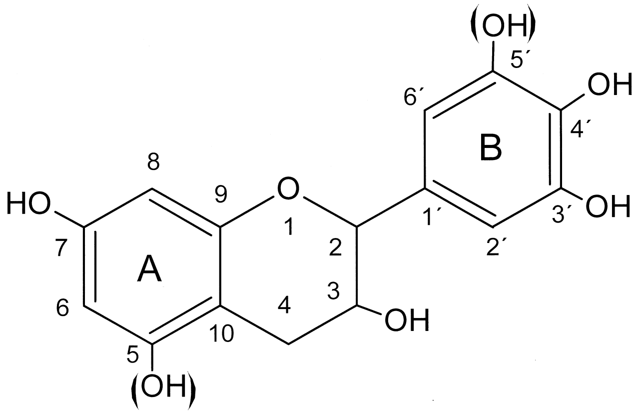

Figure 1 Flavan-3ol repeating unit in polyflavonoid tannin.

EXPERIMENTAL

Materials

The matrix was obtained by crosslinking of a commercial quebracho tannin adhesive, Colatan GT100 (Unitan S.A.I.C., Argentine). This is a fine brown powder used as a 40% (by weight) aqueous solution in the preparation of specimens, according to the usual commercial practice. The hardener was hexamethylenetetramine (HEXA; Mallinckrodt, Argentine), used in a proportion of 10% with respect to the mass of dried adhesive.

The chosen filler was pine woodflour (J. Dos Santos Freire, Buenos Aires, Argentine). All the woodflour particles passed through a 40-mesh sieve (U.S. Standard) and were retained successively by 60-, 100-, and 200-mesh sieves corresponding to average particle sizes of 250 to 420, 150 to 250, and 75 to 150 μm, respectively.

Techniques and testing

Compounding and molding

The composite materials were prepared by mixing the filler and the 40 wt % tannin aqueous solution in an intensive mixer. Improved wetting of the particles was obtained by introducing the hardener (previously dissolved in water) at the end of the mixing step, given that the advance of the crosslinking reaction is minimized with this addition sequence. The resultant powderlike mixture was introduced into a metal mold to be cured under an applied pressure. Because of the initial condition of the mixture, the method used resembles the synthesizing technique of ceramics.

The mixture was cured in a metal mold (diameter: 145 mm; thickness: ~ 3 mm) at 160°C and 4.2 MPa for 30 min. The mold was cylindrical, closed with a piston that applied the load of a heating hydraulic press to the sample. Water vapor as well as some ammonium-containing low molecular weight byproducts were evacuated from the mold, which was not hermetic, but that completely impeded the escape of the solids.

However, it was clear that a fraction of the products of low molecular weight produced in the condensation did not leave the mold and contributed to the formation of microvoids in this process. This "microfoaming," which was distributed throughout the sample, contributed to reduce the overall volumetric contraction and cracking was eliminated. Actually, this has been the goal of using fillers in thermosets for years.

According to the objective of this work, samples were prepared as follows:

1. By maintaining a fixed particle size (75–150 μm) and varying filler contents from 60 to 90% by weight with respect to total composite weight.
2. By maintaining a fixed filler content and varying particle size of the woodflour.

Because of the strong compatibility between the lignocellulosic materials and the chosen matrix, it was not necessary to use any compatibilizing or coupling agents.

Specimens of each sample were dried in a vacuum oven for 72 h at 60°C before testing.

Samples of the unfilled thermoset were prepared to obtain the value of the density of the cured matrix. Microvoiding occasioned by condensation byproducts was of more concern in these samples because contraction during curing was not alleviated by the presence of the woodflour. Thus, two different techniques were used to prepare the samples: (1) the tannin extract powder was mixed with 10% weight of HEXA (dry powders) to promote the condensation; (2) the tannin extract powder was molded to promote self-condensation. In both cases, the reaction was carried out under the same conditions as those used in the preparation of the composite materials. These samples were used only in the determination of the density of the unfilled thermoset of the composites' matrix. The higher value measured for the self-condensated tannin extract was preferred because, given that it produced less-gaseous byproducts, it led to a material without microvoiding.

Microscopy

The efficiency of dispersion during mixing was analyzed using optical microscopy. Scanning electron microscopy (SEM) was used to obtain microphotographs of the fracture surfaces of the wood pine composites (scanning electron microscope Model SEM 505; Philips, The Netherlands). The samples were previously coated with gold.

Author Proof

Thermogravimetric analysis

Thermogravimetric tests were performed using a TGA-50 thermogravimetric analyzer (Shimadzu, Kyoto, Japan) at a heating speed of 10°C/min under air atmosphere.

Dynamic-mechanical tests

Dynamic-mechanical tests were performed using a Perkin–Elmer dynamic mechanical analyzer (DMA 7e, length of specimen platform: 15 mm; Perkin Elmer Cetus Instruments, Norwalk, CT), under a nitrogen atmosphere. The dynamic and static stresses for the material composites were maintained at 400 and 800 kPa and those for the matrix at 200 and 400 kPa, respectively. The frequency of the forced oscillations was fixed at 1 Hz and the heating rate was 10°C/min. The specimens were cut to $20 \times 3 \times 2$ mm^3, and the linear dimensions were measured up to 0.01 mm. At least two replicate determinations were made for each sample to ensure the reproducibility of results.

Moisture sorption

Humid environments were prepared in hermetic containers maintained at 15 ± 2°C in equilibrium with aqueous solutions of sulfuric acid (18 and 35 wt %) to ensure 90 and 60% relative humidity (RH).

Specimens of each sample were dried to a constant weight, determined with an analytical balance (±0.001 g), before exposure to humid environments.

The weight changes, attributed to moisture absorption, were recorded until no further change was detected. All the samples were maintained under these conditions for up to 100 days, a period of time that was sufficiently long enough to reach the equilibrium moisture content (EMC). The measurements were performed on at least four specimens for each sample.

The objective was to determine the percentage moisture content M (percentage weight gain), as manifested by the weight gain of the material as a function of time t:

$$M(t) = \frac{\text{Weight of wet material} - \text{weight of dry material}}{\text{Weight of dry material}} \times 100 \quad (1)$$

The EMC is the $M(t)$ value evaluated at the steady state, usually at the end of the test.

Compression tests

These tests were carried out on dry composites according to ASTM D 695-85. The specimens were cut from the molded plates in the form of prisms of 2.5 mm width and about 5 mm in height. An Instron 8501 universal testing machine (Instron, Canton, MA) was used, and all measurements were performed at a crosshead speed of 2 mm/min. The tests were performed on at least three specimens for each sample.

Flexural tests

Three-point bending tests were performed on wet and dry composites in accordance to ASTM D 790-93 standard (sample type 1) using an Instron 8501 Universal testing machine at a crosshead speed of 2 mm/min. The bending modulus (E_b), ultimate stress (σ_u), and ultimate deformation (r_u) were determined from the stress–strain curves. At least four specimens of each sample were tested.

Composite specimens of approximately $2.5 \times 10 \times 60$ mm^3 were cut from the molded plates for testing.

RESULTS AND DISCUSSION

Morphology analysis

Stiff gels are generally formed at room temperature, by mixing aqueous solutions of tannin adhesive and HEXA.[9] Figure 2(a) and (b) show the results of incorporating HEXA before and after dispersing the filler in the tannin aqueous solution. Incorporating the HEXA hardener before the filler leads to inhomogeneous materials, with gel-like lumps of resin, agglomerating a portion of the particles, while leaving other particles unwetted and generating empty zones (holes) in the material. The addition of HEXA after mixing the filler leads to better dispersion of the particles in the resin solution. Figure 2(b) shows that, in this case, most of the particles are coated by the tannin solution.

The cured material shows good bonding between the woodflour and the matrix. This adhesion could be observed by SEM and is illustrated in Figure 3, which shows the fracture surface of a sample tested in three-point bending. Fiber pull out is scarcely observed, whereas fiber breakage is the most common feature, indicating that there is a good adhesion between the matrix and the fiber.

The lumen of the wood cells appears partially unfilled with the resin because of the high filler concentrations used. The amount of matrix is insufficient to perfectly coat all the individual filler particles and so direct aggregation of wood particles can occur. The matrix presents a microfoamed structure that originated in the condensation reaction of the tannin adhesive with HEXA during the cure molding process. These features have an important effect on the density of the composites. The experimental values were in the range of 1–1.2 g/cm^3, which were lower than the densities predicted using the rule of mixtures as shown:

Author Proof

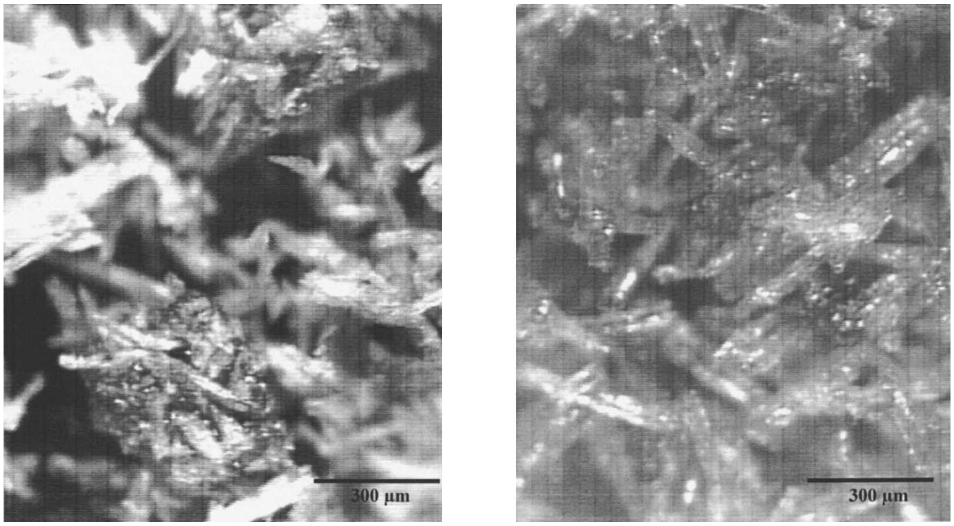

Figure 2 Different photographs showing the tannin/HEXA complex: (a) HEXA incorporated before filler dispersion; (b) HEXA incorporated after filler dispersion.

$$\frac{1}{\rho_{\text{composite}}} = \frac{x_{\text{matrix}}}{\rho_{\text{matrix}}} + \frac{x_{\text{woodflour}}}{\rho_{\text{woodflour}}} \quad (2)$$

where ρ is the density and x is the weight fraction; ρ_{matrix} (1.375 g/cm^3) is the experimental value obtained for the tannin self-condensed resin [this value was used instead of that corresponding to the hexa-crosslinked tannin, which produced a microfoamed matrix of lower density (voiding)]; and $\rho_{\text{woodflour}}$ (1.53 g/cm^3) is taken as the density of the cell wall.[10]

Nico[5] reported experimental density values close to the theoretical predictions for similar composites. However, to prepare these materials very high pressures were used during curing (200–400 bar), which are considerably higher than those used commercially.

Thermal characterization

These tests were carried out on samples of woodflour and tannin adhesive to study their degradation behav-

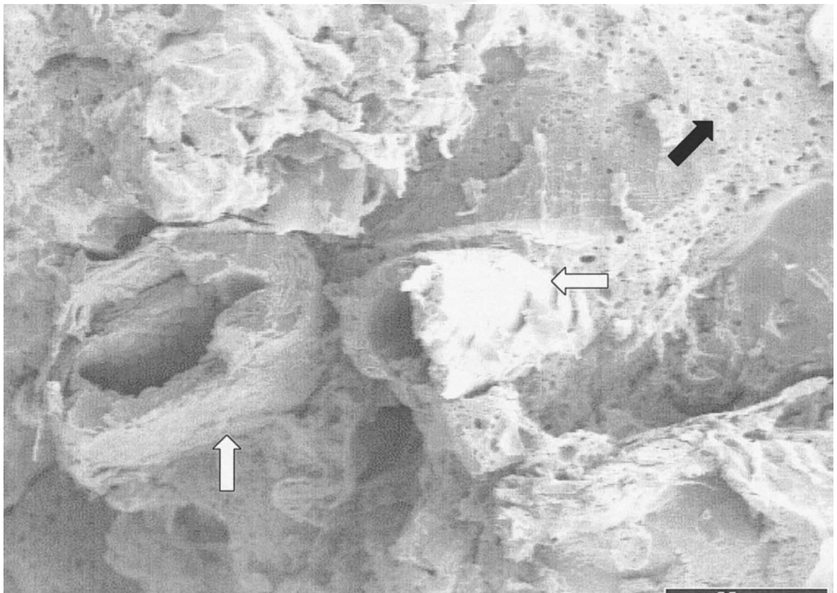

Figure 3 SEM micrographs of the composites (×1000) showing surface fractures from flexural tests. Matrix microvoiding and interphase adhesion are indicated with arrows (black and white, respectively).

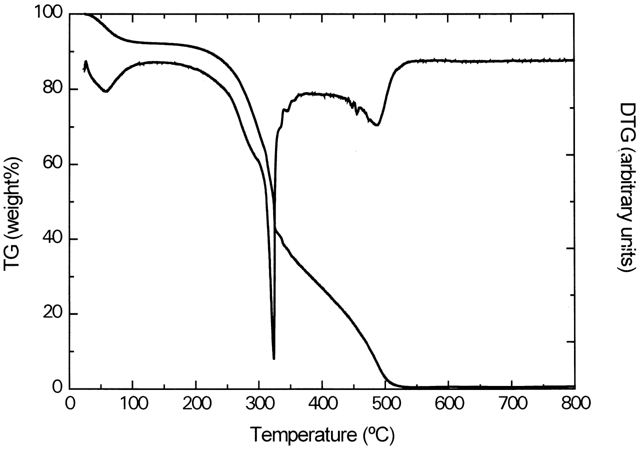

Figure 4 TG (percentage of remaining weight) and DTG (derivative signal) versus temperature curves for woodflour.

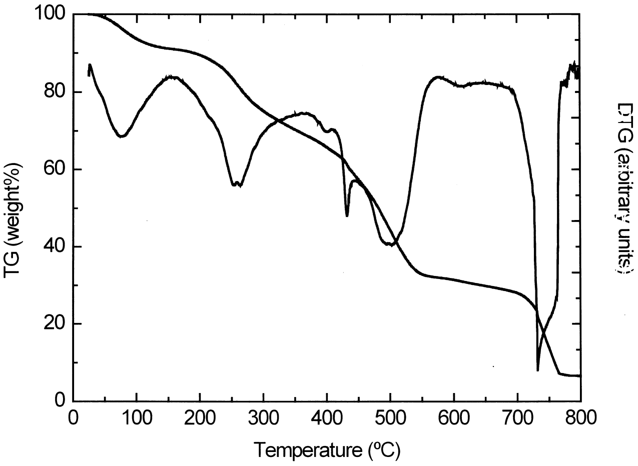

Figure 5 TG (percentage of remaining weight) and DTG (derivative signal) versus temperature curves for tannin adhesive.

ior and to select an optimum molding temperature for curing the samples.

F4 Figure 4 shows that thermal decomposition of woodflour occurs in three main steps: (1) below 100–120°C; (2) in the range of 120 to 350°C; and (3) above 350°C. Similar data were reported for lignocellulosic materials.[11]

The first step corresponds to the loss of absorbed moisture and does not involve degradation of the material. The mass lost (7.7%) is in the same range of the equilibrium moisture content observed in the moisture absorption tests. The second step shows a double peak with maxima at about 270 and 325°C. In this region chain scissions occur and also water molecules are lost as a result of the intramolecular condensation of hydroxyl groups. Finally, in the third step, pyrolitic degradation of the wood components occurs.[12,13]

F5 Figure 5 shows the thermal degradation curve for the tannin adhesive. It is a quite complex curve that shows the initial water loss (9.4% of the original weight), followed by different degradation steps that begin around 200°C. The complex condensed aromatic structure of tannin leads to high thermal resistance. Although wood degradation is almost complete at 500°C, tannin adhesive shows a remaining weight (TG) of about 42%. Actually, the TG curve shows a plateau at about 30%, which extends from 550 to 720°C, where the final degradation step takes place. It is concluded that the tannin adhesive shows remarkable thermal resistance, as is common in phenolic resins.

The glass-transition temperature (T_g) of the tannin adhesive was located at 126°C by differential scanning calorimetry, the same region where T_g appears for pure tannin.[1]

According to the above results, a temperature of 160°C was selected for the curing step. In these conditions the tannin adhesive is above its glass transition, whereas thermal degradation is negligible.

Dynamic mechanical tests

The dynamic mechanical behaviors of the pinewood, the HEXA-crosslinked tannin adhesive, and the composites were evaluated in the bending mode.

Figure 6 shows the storage modulus obtained from temperature scans for the different dry samples. F6

The dynamic modulus of the pinewood shows a very slight increase of the modulus from the beginning of the test to about 120°C. This change is related to the loss of water, which acts as a plasticizer in wood (as discussed in the TGA analysis). The storage modulus E' remains constant from that region up to about

Author Proof

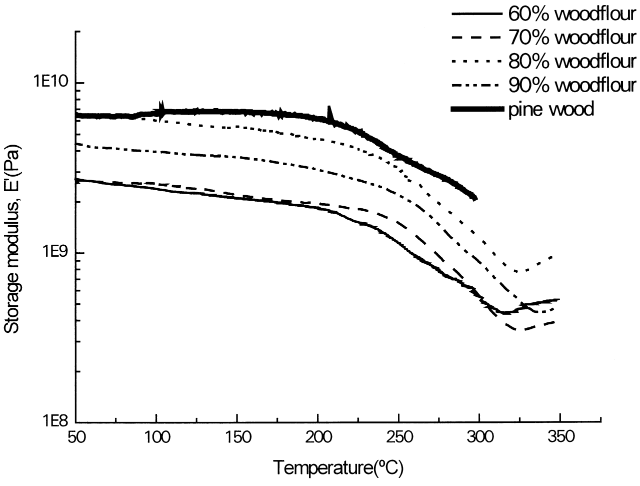

Figure 6 Storage modulus versus temperature for composites prepared with different percentages of filler and pine wood (frequency 1 Hz).

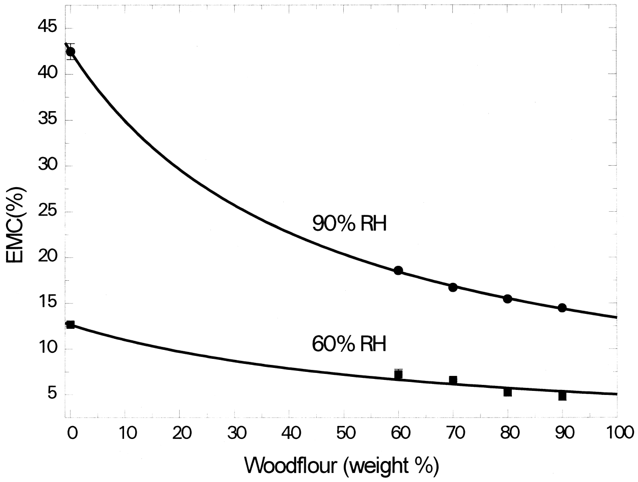

Figure 7 Final (equilibrium) moisture content (EMC) as a function of the wt % of filler at 60 and 90% RH.

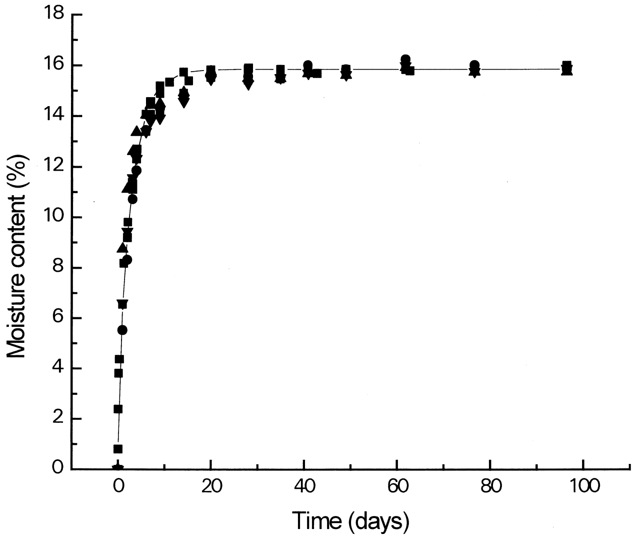

Figure 8 Evolution of moisture content as a function of time at 90 RH for the material loaded with 70 wt % woodflour. Symbols correspond to four replicate samples.

200°C, and then a continuous decrease occurs coincident with the second degradation step in wood.

Because the percentage of wood filler added to the composites is relatively high, all of them show behavior comparable to that of the wood, with the main E' reduction beginning above 200–250°C.

The storage modulus of the composites at room temperature increases as the wood filler concentration is increased from 60 to 80% by weight. The 90% composite shows lower modulus than the 80% sample. The reason for this is the extremely high concentration of particles, which precludes complete particle wetting by the resin, so that the cohesion of the material is compromised. In general, at the concentrations used in this study, direct contact between filler particles is mostly responsible for the load transfer in the composites. Moreover, the particles introduce an elevated degree of mechanical restraint that reduces the mobility and deformability of the matrix.

Moisture absorption

F7 Figure 7 shows the equilibrium moisture content (EMC) reached by the materials as a function of the filler content at 60 and 90% relative humidity. The results show an unexpected reduction of the EMC as more woodflour is added to the material. This unusual behavior is the result of the hygroscopic nature of the tannin matrix, which presents a high proportion of di- and tribenzylamine bridges.[9] These groups are highly polar and favor water absorption. Besides, the filler and the polymeric matrix have an abundance of hydroxyl groups that also contribute to the hygroscopicity.

Moreover, in the case of the tannin matrix, the SEM micrographs show a foamed morphology (Fig. 3), which also increases the capacity of water absorption by diffusion and capillarity effects.

As expected, the higher the ambient humidity, the higher the EMC, given that the driving force for water diffusion absorption increases. It can also be seen that the effect is more important for the unfilled material and becomes more moderate as the woodflour content increases.

The fitted curve was obtained using the following expression:

$$\frac{100}{\text{EMC }\%} = \frac{X_{\text{woodflour}}}{\text{EMC }\%_{\text{woodflour}}} + \frac{X_{\text{matrix}}}{\text{EMC }\%_{\text{matrix}}}$$

$$X_{\text{matrix}} = 1 - X_{\text{woodflour}} \tag{3}$$

where $X_{\text{woodflour}}$ and X_{matrix} are the wt % of woodflour and matrix, respectively.

The EMC of woodflour (EMC$\%_{\text{woodflour}}$) was kept as a fitting parameter of the expression. The resulting values were 5.03 and 13.40 at 60 and 90% RH, respectively, which are in the same order of magnitude as for EMC values reported in the literature for other woodflours[15] and are in agreement with the previous discussion concerning TGA.

Figure 8 shows the typical evolution of the water absorption process as a function of elapsed time. All samples showed a very high initial rate of water absorption, which is revealed by the steep initial slope of the moisture content percentage versus time plots. F8

The rate of moisture absorption was modeled using not only the classical equations for unidirectional diffusion shown below, but also the diffusion coefficient D as a fitting parameter averaged over the whole curve.

Author Proof

TABLE I
Equilibrium Moisture Content for Pine Woodflour of Different Average Particle Sizes

Woodflour (average particle size, μm)	Equilibrium moisture content (%)	
	60 RH	90 RH
250–420	6.14 ± 0.22	15.89 ± 0.05
149–250	6.59 ± 0.31	15.85 ± 0.04
74–149	6.57 ± 0.12	16.71 ± 0.05

The total amount of diffusing substance entered into the sheet at time t (M_t) can be obtained from[16] the following equation:

$$\frac{M_t}{M_\infty} = 1 + \sum_{n=0}^{\infty} \frac{8}{(2n+1)^2\pi^2} \exp\left[\frac{-D\pi^2}{(2l)^2}(2n+1)^2 t\right] \quad (4)$$

where D is the diffusion coefficient, $2l$ is the thickness of the sheet, and M_∞ is the total amount of diffusing substance that had entered into the sheet after an infinite time.

The repeatability of the test was very good as well as the resulting fitting but, because of the steep initial slope, the model has a very low sensitivity to variations in the D parameter. For this reason, although it was not possible to establish a functionality of D with woodflour content, it was possible to calculate a range of values for the diffusion coefficient of the samples between 2×10^{-8} and 9×10^{-8} cm^2/s. These values are of similar in magnitude to those usually reported for wood and similar composites.[15]

The effect of particle size on moisture absorption was initially investigated. Table I shows the results for a composite prepared with 70 wt % of woodflour. Although the average particle sizes used cover a relatively wide range, no significant differences were found in the results. This finding is understandable in view of the contribution of matrix and filler to moisture absorption. Because the matrix is responsible for the major part of the water absorbed in the composite, details of the woodflour particles are not relevant to these results.

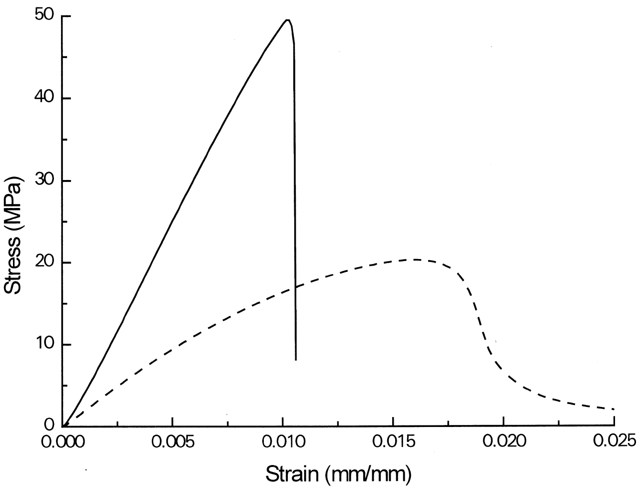

Figure 9 Stress–strain response of the dry (—) and wet (– – –) material with 80 wt % of filler.

Flexural and compression tests

Effect of the filler content

The stress–strain response is linear up to the point of failure for all the dry composites, but shows some bending for the humid materials (Fig. 9). This observation is attributed to the plasticizing effect of water on wood cell wall components and the matrix.

Table II shows the bending modulus (E_b) of the composites as a function of the filler content. The elastic bending modulus increases with increasing woodflour concentration up to 80 wt % and then decreases. The behavior is analogous to that observed in dynamic mechanical tests. As mentioned before, this could be explained by the incomplete wetting of the particles, attributed to the high content of filler used. A similar tendency can be seen in this figure for the ultimate stress as a function of the concentration of woodflour.

TABLE II
Flexural (Bending Modulus, Ultimate Stress, and Ultimate Deformation) and Compressive Properties (Compressive Modulus and Ultimate Stress) as a Function of Neat Woodflour Content for Dry Samples

Woodflour (wt %)	Flexural properties			Compressive properties	
	Bending modulus, E_b (GPa)	Ultimate stress, σ_u (MPa)	Ultimate deformation, r_u (×1000)	Compressive modulus, E_c (GPa)	Ultimate stress, σ_u (MPa)
60	3.49 ± 0.79	31.10 ± 6.65	14.30 ± 4.10	0.91	0.14
70	4.27 ± 0.43	39.51 ± 4.77	10.74 ± 1.68	1.52	0.19
80	4.94 ± 0.37	48.24 ± 9.42	10.13 ± 0.68	2.03	0.48
90	4.41 ± 0.55	35.18 ± 7.32	8.99 ± 0.72	1.03	0.13

Author Proof

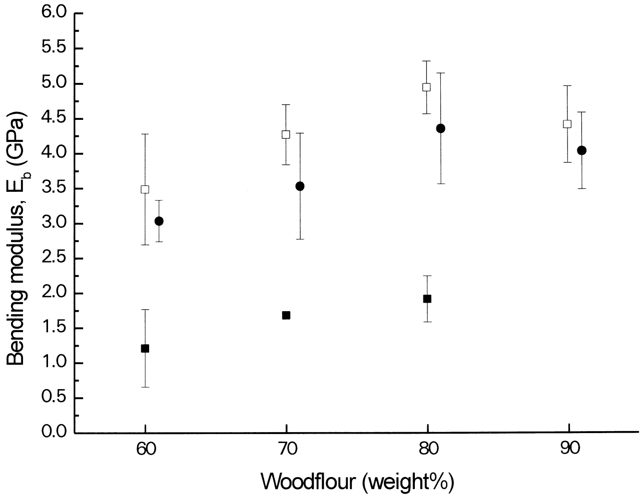

Figure 10 Comparison of flexural properties of dry (■), wet (●), and redried (□) samples for different filler weight percentages: (a) bending modulus (E_b); (b) ultimate stress (σ_u); (c) ultimate deformation (r_u).

As is usually the case, the elongation of the composites decreases with the increase of the filler content in the samples.

It is known that fillers with higher stiffness than that of the matrix can increase the modulus of composites, but generally cause a dramatic decrease in the elongation at break. Almost all the deformation occurs in the matrix, if the filler is more rigid than the matrix. On the other hand, if there is good adhesion between the two components, a decrease of the elongation at break of the composite can be expected.[17,18] In the present case, the mechanical response suggests good adhesion, in agreement with the SEM microscopic observations.

Similar behavior was found in compression tests (Table II). Material failure occurred in the linear part of the curve and no plastic deformation could be observed. This behavior is explained as being the result of combining a rigid matrix with a high concentration of rigid particles.

Figure 10 shows the comparison of the results obtained in three-point bending tests from dry, wet, and redried samples for different filler weight percentages. Regarding the properties of the wet samples at 90 RH (after 100 days), they exhibit an important reduction of the modulus attributed to moisture in the composites. The decrease in E_b for the humid materials can be attributed to two factors: changes in the wood cell wall and matrix plastification. The disruption of highly ordered hydrogen bonds in the wood structure, through formation of less-ordered water–water hydrogen bonds, weakens the resistance of wood to applied stress and thus results in the loss of strength and stiffness as the moisture content increases. It is important to notice that the materials recover, although not completely, after redrying, reaching property values close to those corresponding to the original dry materials. F10

Effect of the particle size

Figure 11 shows the dependency of the flexural mechanical properties with the particle size. The modulus and strength are lower for large size particles, probably because of larger dispersion problems and excessive direct particle–particle contacts. Large particle agglomerates are less effective in transfer load. Decreasing the woodflour particles below a 100-mesh sieve did not produce appreciable changes in the mea- F11

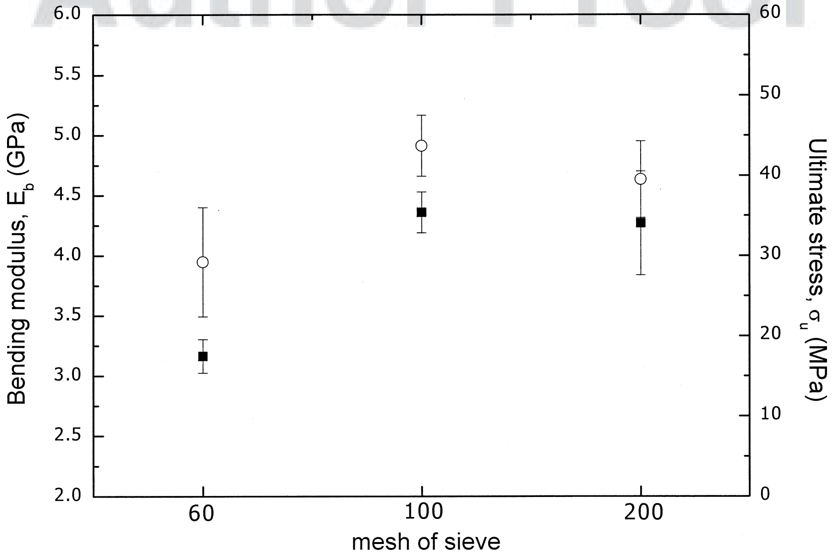

Figure 11 Dependency of the flexural mechanical properties as a function of the particle size. Bending modulus, E_b (■); ultimate stress, σ_u (○).

Author Proof

sured properties, indicating similar dispersion and load transfer characteristics.

Compression tests (not shown) showed identical trends.

CONCLUSIONS

The wetting behavior of woodflour by the aqueous tannin solutions is excellent, leading to very good matrix–fiber adhesion in the composite material.

Fracture surface morphologies show that the matrix, consisting of the cured tannin material, is partially foamed and the lumen of some wood particles is incompletely filled with the matrix material. These two features contribute to lower the experimental density from that corresponding to the compact material predicted by the rule of mixtures.

Flexural and compression mechanical properties reach a maximum at a woodflour concentration of 80%. Above that concentration, these properties diminish because the amount of tannin adhesive is insufficient to wet the fibers uniformly. At a fixed woodflour concentration, the flexural and compression modulus diminish when the size of woodflour particles increases.

The storage moduli of the composite materials have reasonable and constant values up to 200°C. Above this temperature, thermal degradation starts with the consequent deterioration of the properties.

The mechanical properties of the composites are significantly deteriorated because of water absorption. Results show that the cured tannin matrix is more hygroscopic than the woodflour fibers.

The water absorption rate is very high and practically independent of the concentration and size of the woodflour in the composites. This effect is associated with the high polarity of the composite components, matrix microporous structure, and partially empty lumen of fibers.

In the dried state, the thermal and mechanical properties of the investigated woodflour/tannin materials have values adequate for use in some industrial applications where high stiffness is an important requirement. On the other hand this study shows that their use in humid atmospheres must be avoided.

References

1. Pizzi, A. In: Wood Adhesives and Technology; Pizzi, A., Ed.; Marcel Dekker: New York, 1983; Vol. 1, Chapters 3 and 5.
2. Mc Graw, G. W.; Rials, T. G.; Steynberg, J. P.; Hemingway, R. W. In: Plant Polyphenols; Hemingway, R. G.; Laks, P. E., Eds.; Plenum Press: New York, 1992.
3. Pizzi, A.; Tekely, P. J Appl Polym Sci 1995, 56, 1645.
4. Pichelin, F.; Kamoun, C., Pizzi, A. Holz Roh Werkstoff 1999, 57, 305.
5. Nico, R. Plasticos de Tanino deq Uebracho, Laboratorio de Ensayo de Materiales e Investigaciones Tecnológicas-LEMIT, Report 38, Series II, La Plata, Argentina, 1951.
6. Garro Galvez, J. M.; Riedl, B.; Conner, A. H. Holzforschung 1997, 51, 235.
7. Sowunmi, S.; Ebewele, R. O.; Conner, A. H.; River, B. H. J Appl Polym Sci 1996, 62, 577.
8. Marcos, A. E.; Santana, M.; Baumann, G. D. J Wood Chem Technol 1996, 16, 1.
9. Pichelin, F.; Kamoun, C.; Pizzi, A. Holz Roh Werkstoff 1999, 57, 305. AQ: 1
10. Browning, B. L. In: Encyclopedia of Polymer Science and Technology; Bijales, N. M.; Gaylord, N. G.; Mark, H. F., Eds.; Wiley: New York, 1971; Vol. 15, pp. 1–40.
11. Shukry, N.; Girgis, B. S. Polym Plast Technol Eng 1992, 31, 541.
12. Huang, M.-R.; Li, X. G. J Appl Polym Sci 1991, 68, 3205.
13. Flaqué, C.; Montserrat, S. J Appl Polym Sci 1998, 42, 293.
14. García, R.; Pizzi A. J Appl Polym Sci 1998, 70, 1093.
15. Marcovich, N. E.; Reboredo, M. M.; Aranguren, M. I. Polymer 1999, 40, 7313.
16. Crank, J. The Mathematics of Diffusion; Oxford University Press: London, 1970; Chapters IV–VI.
17. Okman, K.; Clemons, C. J Appl Polym Sci 1998, 67, 1503.
18. Marcovich, N. E.; Reboredo, M. M.; Aranguren, M. I. J Appl Polym Sci 1996, 61, 119.

Author Proof

AQ1: Ref. 9 is a duplicate of Ref. 4. Unless there is an alternate entry to replace the duplicate, then Ref. 9 should be deleted and Refs. 10 to 18 will have to renumbered both in the text and in the Reference listing (as 9 to 17).

Author Proof