NRC Publications Archive Archives des publications du CNRC

Comparison between dew-retted and enzyme-retted flax fibers as reinforcing material for composites

Hu, Wei; Ton-That, Minh-Tan; Denault, Johanne; Rho, Denis; Yang, Jianzhong; Lau, Peter C.K.

This publication could be one of several versions: author's original, accepted manuscript or the publisher's version. / La version de cette publication peut être l'une des suivantes : la version prépublication de l'auteur, la version acceptée du manuscrit ou la version de l'éditeur.

For the publisher's version, please access the DOI link below. / Pour consulter la version de l'éditeur, utilisez le lien DOI ci-dessous.

Publisher's version / Version de l'éditeur:

<https://doi.org/10.1002/pen.22060>

Polymer Engineering and Science, 52, 1, pp. 165-171, 2012-01-01

NRC Publications Record / Notice d'Archives des publications de CNRC:

<https://nrc-publications.canada.ca/eng/view/object/?id=e6cff8f8-ede5-4aad-afd2-c0a2d4a8d78e>

<https://publications-cnrc.canada.ca/fra/voir/objet/?id=e6cff8f8-ede5-4aad-afd2-c0a2d4a8d78e>

Access and use of this website and the material on it are subject to the Terms and Conditions set forth at

<https://nrc-publications.canada.ca/eng/copyright>

READ THESE TERMS AND CONDITIONS CAREFULLY BEFORE USING THIS WEBSITE.

L'accès à ce site Web et l'utilisation de son contenu sont assujettis aux conditions présentées dans le site

<https://publications-cnrc.canada.ca/fra/droits>

LISEZ CES CONDITIONS ATTENTIVEMENT AVANT D'UTILISER CE SITE WEB.

Questions? Contact the NRC Publications Archive team at

PublicationsArchive-ArchivesPublications@nrc-cnrc.gc.ca. If you wish to email the authors directly, please see the first page of the publication for their contact information.

Vous avez des questions? Nous pouvons vous aider. Pour communiquer directement avec un auteur, consultez la première page de la revue dans laquelle son article a été publié afin de trouver ses coordonnées. Si vous n'arrivez pas à les repérer, communiquez avec nous à PublicationsArchive-ArchivesPublications@nrc-cnrc.gc.ca.

National Research
Council Canada

Conseil national de
recherches Canada

Canada

Comparison Between Dew-Retted and Enzyme-Retted Flax Fibers as Reinforcing Material for Composites

Wei Hu,¹ Minh-Tan Ton-That,¹ Johanne Denault,¹ Denis Rho,² Jianzhong Yang,² Peter C.K. Lau²

¹ Industrial Materials Institute, National Research Council of Canada, 75, de Mortagne, Boucherville, Québec, Canada J4B 6Y4

² Biotechnology Research Institute, National Research Council Canada, Montréal, Québec, Canada H4P 2R2

Two kinds of retted Canadian linseed flax fibers, dew-retted (F1) and enzyme-retted flax fibers (F2) were characterized in detail for their applications in composites, such as retting degree, thermal stability, tensile strength, and interfacial behavior in polypropylene (PP) matrix. It's clear from Scanning Electron Micrograph that the aspect ratio of F2 was much higher than that of F1 in the light of their separated elementary fibers in most cases. Instead, the elementary fibers of F1 remained tightly bundled into technical fiber wrapping with more non-cellulose portions. This reflected its lower retting degree and resulted in its lower thermal stability. Single fiber tensile test and single fiber pull-out test were used to evaluate the fiber tensile properties and fiber/PP interfacial shear strength, respectively. Better retting degree and fewer damages on F2 endowed F2 better tensile property. Consequently, higher aspect ratio, retting degree, and tensile strength proved F2 to be a kind of better reinforcing material than F1 for composites. POLYM. ENG. SCI., 00:000-000, 2011. 2011 published by Society of Plastics Engineers*

INTRODUCTION

Nowadays, more and more attention has been paid to natural fiber reinforcing polymer composites in the field of material research in order to achieve good mechanical properties, low abrasion, environmental friendliness, and low-cost objectives [1, 2]. It has been reported that the wood fiber and nonwood fiber plastic composites are kinds of promising and sustainable green material [3–5]. Even waste agricultural residues, such as sun-flower stalk, corn stalk, and bagasse fibers could be used as reinforcement for thermoplastics [6]. Among natural fibers, flax fibers have also been widely used as reinforcing materials for

composites [7–20]. In general, flax straw consists of a composite of technical fibers and binder based on pectin, lignin, and hemicelluloses. These fibers mainly locate near the outer layer of the straw. One technical fiber is composed of several so-called elementary fibers, bundled together by pectin and lignin, etc. The process to remove the binding substances, such as pectin and lignin from the fiber bundle to release the individual fibers and increase the fiber strength is called retting process. This process is usually microbial in nature, to loose and separate the bast fiber bundles from the non-fiber fractions of the flax stem [11].

Retting process can involve water treatment, dew-retted treatment [10–13], and enzyme treatment [14–20]. The research challenge is to avoid the individual fiber damage during this process and to keep the process at low cost and sustainable. The water retting process takes long time, and always results in a serious ecological problem. Dew retting is limited to geographic regions where temperature and humidity must be suitable for fungal activities. The obtained fibers are not consistent in fiber characteristics. Also the mechanical property of flax fiber obtained from the dew retting is poorer and coarser than that obtained from water retting. In addition, it requires occupation of agricultural fields for some weeks [14, 17]. Recently, enzyme retting has been demonstrated as a promising replacement for traditional retting methods for its time-saving, ecology friendliness, and convenient characteristics. Some kinds of enzyme, such as Flaxzyme, are reported to produce fibers with good yield and quality, which is similar to those obtained from high-quality water retting process [16].

Weyenberg et al. [21] proposed that composite properties can increase with the retting degree by better interface due to the reduction of non-cellulose portions left on fiber surface, and also by the higher fiber aspect ratio due to the extent of the separation of elementary fibers [22, 23]. Better retting degree means the elementary fibers are released well from the technical fibers and separated from each other with less non-fiber tissue attached on the surface. In such case, the aspect ratio (length/diameter) of

Correspondence to: Minh-Tan Ton-That; e-mail: Minh-Tan.Ton-That@imi.nrc-nrc.gc.ca

Contract grant sponsors: Agriculture and Agri-food Canada; National Research Council Canada.

DOI 10.1002/pen.22060

Published online in Wiley Online Library (wileyonlinelibrary.com).

© 2011 Crown in the right of Canada

fibers must be significantly increased. When retting degree is low, impurities (pectin, lignin, hemicelluloses, etc.) between the fibers can cause stress concentrations in composite and lead to early fracture [21]. An optimal retting process affords optimum retting degree and composite properties.

Fibers recovered from linen flax varieties have been well characterized and also applied in composite applications, while the fibers from linseed flax varieties typically grown in Canada are not so well studied [24–29]. In this work, the retting degree of dew-retted linseed flax fiber (F1) was characterized in details, in comparison with that of enzyme-retted linseed flax fiber (F2), for their potential application as reinforcing materials. The single fiber tensile test (SFTT) and single fiber pull-out test (SFPT) were conducted to characterize the fiber tensile properties and fiber-matrix interfacial behavior. Transcrystallization phenomenon of PP at the surface of dew- and enzyme-retted fibers was studied to further illustrate the effect of the retting degree on the composite morphology.

EXPERIMENTAL

F1 was kindly supplied by Schweitzer-Mauduit Company, and F2 was prepared in the laboratory following the procedure described previously [28]. Homopolypropylene Pro-fax PDC 1274 (PP) (weight-average molecular weight is 250 kg mol^{-1}) was obtained from Basel and used as the matrix for the composites.

Scanning Electronic Microscopy (SEM)

A JEOL JSM-6100 SEM at a voltage of 10 kV was utilized to observe the fiber surface and also fiber bundle cross-section to characterize the retting degree. Before SEM observation, the samples were coated with Au/Pd to ensure good conductivity.

Thermal Analysis

The thermal stability of the flax fibers was measured on a TG 96 SETRAM TGA. The measurements were carried out from 25 to 700°C at a heating rate of $20^\circ\text{C min}^{-1}$ in inert nitrogen gas.

SFTT

The tensile properties of the fibers were evaluated according to the procedure described previously [29].

SFPT

Since the stress transfer from matrix to the fiber through interface in composites, the quality of the fiber/matrix interface is one of important factors which control overall mechanical properties of composites system. The apparent interfacial shear strength (τ_{IFSS}) could afford the information of interface adhesion. SFPT is one of the

FIG. 1. Scheme of preparing the sample for sing fiber pull-out test.

widely applied methods to characterize the interfacial adhesion between the fiber and polymer matrix [30–37]. τ_{IFSS} was calculated from the maximum load (F_{max}) required to debond the fiber from the matrix and fiber embedded area (A_e), as shown in equation: $\tau_{\text{IFSS}} = F_{\text{max}}/A_e$. [31]. Most people obtained the A_e value according to the equation: $A_e = L_e \times D \times \pi$, where L_e is the fiber embedded length and D is the fiber diameter [31–35]. The method to determine L_e and D varied with different researchers and the τ_{IFSS} results were always with high standard deviation. To obtain the accurate shear strength of interface, a practical SFPT was explored in this work by more accurate determination of L_e and A_e applying optical microscopy (OM) and SEM observations, respectively. The procedures are described here in detail for the first time.

Flax fiber with uniform end was selected carefully after observation under the polarized optical microscopy (POM: Leitz WETZLAR DIALUX 20 Polarized Optical Microscopy installed with CoolSNAP-Procf Color camera). Then it was stuck on a piece of rectangular glass with the end sticking outside of glass edge for about $200 \mu\text{m}$ with the aid of the POM. A piece of rectangular PP film with a thickness of 1 mm was first kept at 200°C for 10 min on a hot stage to fully melt. Then, fiber end was embedded into the matrix when its attached glass approaching to the melt PP. Figure 1 illustrates the scheme of this procedure. The role of glass was to control the L_e and keep the fiber perpendicular to the matrix. The L_e was measured precisely using the OM image of the specimen taken before and after the pull-out test (see Fig. 2).

The SFPT test was performed using an Instron 5548 Microtester machine with a speed of 0.1 mm s^{-1} . The apparent interfacial shear strength (τ_{IFSS}) was calculated from the maximum load (F_{max}) required to debond the fiber from the matrix and A_e , as shown in equation: $\tau_{\text{IFSS}} = F_{\text{max}}/A_e$ [30]. A_e is calculated accurately by multiplying the fiber perimeter P_e , which was measured directly from the SEM image of the imprint the fiber left in the matrix, with the L_e . Figure 3 shows the imprint image obtained from SEM observation of F2 after the fiber was pulled out from the matrix. From this image, the borderline of the imprint is traced out using the Adobe Photoshop 4.0 LE software. Finally, the accurate value of perimeter can be obtained automatically using Image-pro Plus 4.5.1.27 software according to

FIG. 2. OM images: (a) before and (b) after the fiber pulled out from PP matrix.

the borderline. The samples with the technical fibers partially and uncontrollably failed inside the matrix were not considered into calculation of τ_{IFSS} .

Trycrystallization

The F1 and F2 fibers were aligned on a piece of PP films with a thickness of 0.04 mm. Then, both systems

FIG. 3. SEM image from top view of imprint image of F2 fiber after pull-out test.

were placed onto a pressing machine, which the temperature was set at 190°C. The systems were kept for 5 min at this temperature to obtain the complete melting of the PP. Thereafter, the power was shut down to decrease temperature in the air with a holding pressure of about 2 MPa to make the film thickness to be about 0.02 mm. Leitz WETZLAR DIALUX 20 Polarized Optical Microscopy installed with CoolSNAP-Procf Color camera was used to observe the transcrystallization of PP on the fiber surface in the obtained samples.

RESULTS AND DISCUSSION

Retting Degree

Figure 4 shows the SEM images of F1 and F2 surface. It can be seen from Fig. 4a that most elementary fibers of F1 were still bundled together and wrapped by a thick layer of pectin and lignin at many different locations along the fibers. This indicates that the fibers were well decorticated but not fully, and the fibers were not pure cellulose. It may be due to the fact that fungal activity of

FIG. 4. SEM images of F1 and F2 technical fibers: (a) F1 fiber bundles attached with thick pectin, lignin, etc; (b) separated elementary F2 fibers with much less pectin and lignin, etc.

FIG. 5. Thermal analysis curves for F1 and F2: (a) TGA and (b) DTG.

dew-retting is a natural process which could not be well controlled and happen uniformly on the stems during retting process [10, 11]. On the other hand, Fig. 4b shows almost completely separated elementary fibers of F2 with much less pectin and lignin cuticles on their surface. As a consequence, the aspect ratio of F2 should be expected to be higher than that of F1. In addition, smoother fiber surfaces can be observed for most parts on F2 as only a certain small portion of pectin and lignin adhered on the F2 surface. Similar observations have been reported for enzyme-retted fibers [15]. It could be concluded here that, the retting degree of F2 is better than that of F1 in the light of its higher elementary fiber separation extent and much less non-cellulose part left on fiber surface. Thus, the enzyme retting process was proved to be more efficient than the dew retting process.

TABLE 1. Thermogravimetric analysis of dew- and enzyme-retted fibers.

	5% Weight loss temperature (T_5) (°C)	10% weight loss temperature (T_{10}) (°C)	Max. degradation temperature (°C)
F1	216.0 ± 0.5	278.2 ± 0.7	354.5 ± 0.6
F2	275.7 ± 0.6	314.6 ± 0.5	359.2 ± 0.6

It could also be observed in Fig. 4 that more kinks and nodes or damages were observed along the fiber surface for F1 (the naked fiber in Fig. 4a) than for F2 (Fig. 4b). These kinks or nodes may be attributed to the fiber cell tip overlap and also damage caused by the mechanical force during the decorticating process [38, 39]. Such defects may have negative effect on the flax fiber mechanical properties, which will be discussed later.

Thermal Stability

Thermal degradation behavior for F1 and F2 fibers are shown in Fig. 5. It is interesting to observe that the TGA curve (Fig. 5a) of F1 lies below that of F2, and the temperature of DTG peak (Fig. 5b) is lower for F1. This indicated that F2 has better resistance to thermal degradation than F1. Table 1 summarized the decomposition temperature differences for F1 and F2 as extracted from Fig. 5. In general, there was less than 5% of weight loss for both F1 and F2 until 140°C which is mainly due to the humidity in fibers. Thereafter, F2 presented higher T_5 , T_{10} , and T_{max} than those of F1. In particular, their difference of T_5 and T_{10} was very significant, which is as large as 60 and 30°C, respectively. Such difference proved F1 degraded at lower temperature than F2. This is supposed to be resulted by the higher content of non-cellulose portions of F1 as shown in Fig. 4, in the light that the thermal stability of non-cellulose portions, such as pectin, lignin, hemicellulose is lower than that of cellulose [40]. Such a fact proved another advantage of F2 in terms of thermal degradation resistance, besides its higher aspect ratio and greater purity. The final chars were the same in both samples confirming the impurities observed on both F1 and F2 surface was mainly organics.

Tensile Strength of Fiber

Typical stress-strain curves of flax fiber could be referred in Ref. 29. Though there was a little slippage, flax fibers exhibited essentially linear or Hookean region, then a sharp drop in strength after reaching the maximum. Both of F1 and F2 showed brittle failure. With the improved SFTT method [29], accurate tensile strength of F1 and F2 was obtained. The mechanical properties data of F1 and F2 are shown in Table 2. The strength of F2 (489 ± 34 MPa) is higher than that of F1 (399 ± 20 MPa). And the modulus of F2 (57 ± 5 GPa) is also higher than that of F1 (46 ± 4 GPa). It is known that the cuticle on fiber surface mainly consisted of pectin and

TABLE 2. Calculated tensile strength, modulus, strain, and interfacial shear strength values of dew- and enzyme-retted fibers.

	Strength (MPa)	Modulus (GPa)	Strain (%)	τ_{IFSS} (MPa)	L_c (mm)
F1	399 ± 28	46 ± 4	2.03 ± 0.84	6.3 ± 0.6	3.57
F2	489 ± 34	57 ± 5	2.08 ± 0.68	5.7 ± 0.5	3.70

FIG. 6. Typical pull-out test curve of flax/PP system.

lignin contributes artificially on the cross-section area, thus decreases the tensile strength of fiber. As shown earlier, F1 has more pectin and lignin on the fiber surface. It is not surprising to see that mechanical property of F1 is lower than that of F2. In addition, SEM observations (see Fig. 4) reveal the more kinks, nodes, and damages in F1 than in F2. It is expected that such severe defects could result in premature failure during stress suppressing process in the mechanical test, thus leading to the loss of fiber mechanical properties. The more naked elementary fibers with less portion of pectin and lignin and less kinks and defects on fibers should account for the better mechanical property of enzyme-retted fiber F2. This confirms again the enzyme retting process is promising in regards of its potential utilization for natural fibers as composite reinforcement.

Interfacial Adhesion

A representative example of load-displacement curves obtained from the pull-out test of flax fiber/PP composites is shown in Fig. 6. All the samples showed similar characteristic and stable behavior during pull-out test. In general, there was an initial increase of load with displacement which is characteristic of elastic bonding at the fiber-matrix interface. After reaching the maximum debonding load, $F_{\max}$, the fiber was pulled out stably and showed a smooth transition until it was completely pulled out.

Figure 7a shows the relationship between the apparent shear strength τ_{IFSS} and embedded length L_e for F1 and F2. This relationship provide the information of brittle or ductile fracture behavior [30, 34, 36]. It could be observed from Fig. 7a that τ_{IFSS} decreased with increasing L_e , which proved brittle failure behavior for both F1 and F2. Figure 7b plotted the maximum load during the pull-out test versus the embedded fiber area (A_e) for F1 and F2. The slope of the linear fit of each set of data was considered to be the average τ_{IFSS} value. The linear regression was forced through zero because no force was

required when fiber is not embedded in the matrix [30, 33]. The τ_{IFSS} value obtained for F1 and F2 are 6.3 ± 0.6 and 5.7 ± 0.5 MPa, respectively (Table 2). It's obvious that our newly developed SFPT approach can produce precise τ_{IFSS} result with much lower standard deviation compared with the literatures as reflected in the error bar [30–35]. More accurate determination of L_e and A_e applying OM and SEM observation mainly contribute to this improvement. The absolute value of τ_{IFSS} for F1 is slightly higher than that of F2. This difference became negligible when the SD was taken into account. This was possibly resulted from the rougher surface of F1 (as shown in Fig. 4a) that increases the contact area between fiber and matrix and also resulted in more interlocking and hence greater friction forces during the pull-out process. It should be noted here that the adhesion is not only controlled by the fiber chemistry, but also the fiber surface topology.

Transcrystallization (TC)

It is well known that the fiber embedded in PP matrix can act as a nucleating agent for the growth of spherulites [41]. When there are many nucleating sites along the fiber

FIG. 7. (a) Apparent interfacial shear strength as function of L_e ; (b) The maximum pull-out force as function of the embedded fiber area (A_e).

FIG. 8. POM images of the TC layer in: (a) F1/PP composites and (b) F2/PP composites.

surface the spherulite growth could be restricted in the lateral direction of the fiber. As a result, a columnar layer called TC will grow from the fiber surface [41–46]. The roughness of fiber surface or topology is supposed to be responsible for the nucleation. It is generally considered that the transcrystalline layer at the fiber–matrix interface has significant effect on the mechanical performance of fiber-reinforced composite materials [41–43, 46].

Figure 8 shows the POM micrographs of F1/PP and F2/PP composites. Both of them presented the characteristic phenomenon of TC: dense heterogeneous nucleation of the matrix crystals on the fiber surface growing perpendicular to the fiber axis, with the growing front impinged with the spherulites nucleated in the bulk of the matrix. It can also be observed that the TC layer around F1 surface (Fig. 8a) seemed thicker and more uniform than those around F2 surface (Fig. 8b) across different specimens.

It was reported that the presence of lignin and hemicelluloses on fiber surface inhibits transcrystallization [44]. However, the level of surface roughness (or surface topology), such as small-scale grooves could generate thermal stress concentration during consolidation, thus enhance the nucleating process of transcrystallization [45, 46]. From our results, it seemed that the fiber surface rough-

ness dominate the difference in lignin and hemicellulose content between dew- and enzyme-retted fibers. The greater roughness of F1 fiber surface resulted in thicker transcrystallization. This roughness was related to the cuticles attached on F1 fiber bundle surface, which proved the retting degree of F1 was low.

Critical Length

The critical fiber length (L_c) could be defined as the minimum fiber length required to transfer enough stress from matrix to fiber via interface, so that fiber break. L_c is a function of the properties of reinforcement and the fiber–matrix interface, and could be used to estimate the fiber length distribution of composites [37, 47]. It provides the essential information of the length at which the fiber achieves the maximum stress by the fiber and matrix interface. It could be calculated according to the Eq. 1:

$$L_c = \sigma_f r_f / \tau_{IFSS} \quad (1)$$

where σ_f is the fiber tensile strength and r_f is the fiber radius. In this work, σ_f could be determined in the SFTT, r_f was determined using the equation of $r_f = P_c / 2\pi$, where fiber perimeter P_c was determined by SEM observation, and τ_{IFSS} was obtained in SFPT tests. The L_c data of F1 and F2 is also shown in Table 2. For better understanding of critical length, for example, when F1 fiber length is shorter than its L_c 3.57 mm, the bond between fiber and PP matrix would be broken and the fiber could be extracted before fracture; if F1 fiber length is longer than 3.57 mm, the fiber could be stressed until fracture without being pulled out from matrix. Both L_c value of F1 and F2 are higher than that reported in Ref. 47, which maybe mainly because of the different source of flax with different size applied.

CONCLUSIONS

The aspect ratio, retting degree, tensile strength, transcrystalline, and interface behavior of dew- and enzyme-retted fibers were characterized contrastively for their promising application in composites as reinforcing material. SEM observations showed that there were more separated elementary fibers in F2, which contributed to its higher aspect ratio than that of F1. The surface of F1 was rougher than that of F2. This rougher surface was mainly consisted of non-cellulose portions, such as pectin, lignin, and hemicelluloses. This provided an explanation for its lower thermal stability than that of F2. Therefore, the retting degree of enzyme-retted fibers was concluded to be better than that of dew-retted fibers, according to its much more separated elementary fibers and less amounts of pectin and lignin on the fiber surface. Tensile strength for F2 was 489 ± 34 MPa, which was higher than that of F1 (399 ± 28 MPa). This could be contributed from less defects and better retting degree of F2. Although the

rougher surface of F1 resulted in a more uniform and thick transcrystalline in F1/PP composites, and also a slightly higher interfacial shear strength value of 6.3 ± 0.6 MPa (for F2, τ_{IFSS} is 5.7 ± 0.5 MPa), enzyme-retted flax was appeared to be a kind of better reinforcing material than dew-retted flax for composites because of its higher aspect ratio, better-retting degree, less impurity and defects, and greater tensile properties.

REFERENCES

1. A.K. Bledzki and J. Gassan, *Prog. Polym. Sci.*, **24**, 221 (1999).
2. S.V. Joshi, L.T. Drzal, A.K. Mohanty, and S. Arora, *Compos. A*, **35**, 371 (2004).
3. A. Ashori, *Bioresol. Technol.*, **99**(11), 4661 (2008).
4. A. Nourbakhsh, A. Ashori, and M. Kouhpayehzadeh, *Reinforce. Plast. Compos.*, **28**(17), 2143 (2009).
5. A. Ashori and Z. Bahreini, *Compos. Mater.*, **43**(11), 1297 (2009).
6. A. Ashori and A. Nourbakhsh, *Waste Manage.*, **30**(4), 680 (2010).
7. A. Arbelaiz, B. Fernández, G. Cantero, R. Llano-Ponte, A. Valea, and I. Mondragon, *Compos. A*, **36**, 1637 (2005).
8. M.J.A. Van den Oever, H.L. Bos, and K. Molenveld, *Die Angew. Makromol. Chem.*, **272**, 71 (1999).
9. G. Romhány, J. Karger-Kocsis, and T. Czigány, *J. Appl. Polym. Sci.*, **90**, 3638 (2003).
10. W.H. Morrison III, D.D. Archibald, H.S.S. Sharma, and D.E. Akin, *Ind. Crop. Prod.*, **12**, 39 (2000).
11. D.E. Akin, *Industrial Applications of Natural Fibres: Structure, Properties and Technical Applications*, Chapter 4, Wiley, Chichester (2010).
12. B.E. Pallesen, *Ind. Crop. Prod.*, **5**, 65 (1996).
13. H.S.S. Sharma and G.J. Faughey, *Ann. Appl. Biol.*, **135**, 495 (1999).
14. D.E. Akin, W.H. Morrison, L.L. Rigsby, J.D. Evans, and J.A. Foulk, *Ind. Crop. Prod.*, **17**, 149 (2003).
15. D.E. Akin, B. Condon, M. Sohn, J.A. Foulk, R.B. Dodd, and L.L. Rigsby, *Ind. Crop. Prod.*, **25**, 136 (2007).
16. C.F. Van Sumere and H.S.S. Sharma, *Aspects Appl. Biol.*, **28**, 15 (1991).
17. D.E. Akin, J.A. Foulk, R.B. Dodd, and D.D. McAlister III, *J. Biotech.*, **89**, 193 (2001).
18. J.A. Foulk, W.Y. Chao, D.E. Akin, R.B. Dodd, and P.A. Layton, *J. Polym. Environ.*, **12**(3), 165 (2004).
19. J. Marek, V. Antonov, M. Bjelkova, P. Smirous, H. Fischer, and S. Janosik, *2008 International Conference on Flax and Other Bast Plants*, Saskatoon, Canada, 159 (2008).
20. C. Mooney, T. Stolle-Smits, H. Schols, and E. de Jong, *J. Biotech.*, **89**, 205 (2001).
21. I.V.D. Weyenberg, J. Ivens, A.D. Coster, B. Kino, E. Baetens, and I. Verpoest, *Compos. Sci. Technol.*, **63**(9), 1241 (2003).
22. G. Fila, L.M. Manici, and F. Caputo, *Ann. Appl. Biol.*, **138**, 343 (2001).
23. A.K. Mohanty, M. Misra, and L.T. Drzal, *Natural Fibers, Biopolymers, and Biocomposites*, Chapter 4, Taylor & Francis, New York (2005).
24. X. Li, S.A. Panigrahi, and L.G. Tabil, *Appl. Eng. Agric.*, **25**(4), 525 (2009).
25. D.E. Akin, W. Herbert Morrison III, L.L. Rigsby, and R.B. Dodd, *J. Agric. Food Chem.*, **49**, 5778 (2001).
26. X. Li, S.A. Panigrahi, L.G. Tabil, and W.J. Crerar, *2004 North Central ASAE/CSAE Conference*, Winnipeg, Canada, MB04-305 (2004).
27. M. Alcock, M. Fuqua, C. Ulven, E. Kerr-Anderson, and J. Foulk, *2008 International Conference on Flax and Other Bast Plants*, Saskatoon, Canada, 258 (2008).
28. D. Rho, J. Yang, P.C.K. Lau, W. Hu, M.-T. Ton-That, and J. Denault, *Conference Innovation*, Montreal, Canada (2008).
29. W. Hu, M.T. Ton-That, F. Perrin-Sarazin, and J. Denault, *Polym. Eng. Sci.*, **50**(4), 819 (2010).
30. A. Baltazar-y-Jimenez, M. Bistriz, E. Schulz, and A. Bismarck, *Compos. Sci. Technol.*, **68**, 215 (2008).
31. S. Wong, R.A. Shanks, and A. Hodzic, *Compos. Sci. Technol.*, **67**, 2478 (2007).
32. Y. Li and Y.W. Mai, *J. Adhes.*, **82**, 527 (2006).
33. J. Morales, M.G. Olayo, G.J. Cruz, P. Herrera-Franco, and R. Olayo, *J. Appl. Poly. Sci.*, **101**, 3821 (2006).
34. A. Stamboulis, C. Baillie, and E. Schulz, *Die Angew. Makromol. Chem.*, **272**, 117 (1999).
35. M.A. López Manchado, M. Arroyo, J. Biagiotti, and J.M. Kenny, *J. Appl. Polym. Sci.*, **90**, 2170 (2003).
36. R.V. Subramanian, J.J. Jakubowski, and F.D. Williams, *J. Adhes.*, **9**, 185 (1978).
37. A. Kelly and W.R. Tyson, *J. Mech. Phys. Solids*, **13**(6), 329 (1965).
38. C. Baley, *J. Mater. Sci.*, **39**, 331 (2004).
39. G.C. Davies and D.M. Bruce, *Text. Res. J.*, **68**(9), 623 (1998).
40. M.V. Ramiah, *J. Appl. Polym. Sci.*, **14**, 1323 (1970).
41. N.E. Zafeiropoulos, C.A. Baillie, and F.L. Matthews, *Compos. A*, **32**, 525 (2001).
42. H. Quan, Z.M. Li, M.B. Yang, and R. Huang, *Compos. Sci. Technol.*, **65**, 999 (2005).
43. A. Arbeiliz, B. Fernandez, J.A. Ramos, and I. Mondragon, *Thermochim. Acta*, **440**, 111 (2006).
44. D.G. Gray, *J. Polym. Sci. Polym. Lett. Ed.*, **12**, 509 (1974).
45. C. Wang and C.R. Liu, *Polymer*, **40**(2), 289 (1999).
46. G. Sanjeev, W. Bart, G. Jayamol, S. Nattakan, and P. Ton, *J. Mater. Sci.*, **44**, 510 (2009).
47. T. Aurich and G. Mennig, *Adv. Compo. Lett.*, **10**(6), 299 (2001).