Available online at www.sciencedirect.com
ScienceDirect
Carbohydrate Polymers 71 (2008) 458–467
Carbohydrate Polymers
www.elsevier.com/locate/carbpol

The effect of fibre volume fraction and mercerization on the properties of all-cellulose composites

Chen Qin [a,b], Nattakan Soykeabkaew [a], Ni Xiuyuan [b], Ton Peijs [a,*]

[a] *Department of Materials, Queen Mary, University of London, London E1 4NS, UK*
[b] *Department of Macromolecular Science, Fudan University, Shanghai 200433, China*

Received 20 November 2006; received in revised form 30 April 2007; accepted 18 June 2007
Available online 4 July 2007

Abstract

All-cellulose composites with 85–95% fibre volume fraction were successfully prepared by using solutions of 1–7% (wt/v) cellulose concentrations (dissolved ligno-cellulosic ramie fibres in LiCl/DMAc) for impregnation of aligned ramie fibres. The effect of mercerization or alkali treatment to the properties of the prepared composites was also investigated. The structure, morphology, and mechanical properties of the composites were characterized by scanning electron microscopy, X-ray diffraction, Raman spectroscopy, and tensile testing. After mercerization, tensile strength of the prepared composites was improved by 15–95%. The optimal all-cellulose composite, was based on a cellulose matrix obtained from a 4% cellulose concentration in solution, which led to a fibre volume fraction of 85%, resulting in an optimal combination of a sufficient amount of matrix phase with good fibre wet-out due to a low matrix viscosity and a high tensile strength due to a high fibre volume fraction. Alkali treatment successfully further improved the tensile strength of these composites from 440 MPa for un-mercerized composites to 540 MPa for mercerized composites, which are values that compare very favourable to more traditional random and unidirectional natural fibre based composites. Raman spectroscopy indicated that orientation of the aligned ramie fibres in the mercerized composites is well-maintained. X-ray diffraction confirms that native cellulose I, which is the major polymorphic modification of cellulose in these composites, is rearranged to cellulose II crystal packing after mercerization.

Keywords: All-cellulose composites; Fibre volume fraction; Mercerization; Mechanical properties

1. Introduction

Recent trends towards environmentally friendly polymer composite systems have been focussing on the use of ligno-cellulosic fibres such as flax, hemp, ramie, or sisal as a replacement for glass fibres (Garkhail, Heijenrath, & Peijs, 2000; Peijs, 2002). These natural fibres have some ecological advantages over glass fibres since they are renewable and can be incinerated. Alternative routes to environmentally friendly polymer composites have focussed on a different approach; so-called single polymer composites or self-reinforced polymer composites, which follow mono-material based *eco-design* concepts. All-polypropylene composites have been proposed to replace traditional glass fibre reinforced plastics for a number of applications, notably the automotive industry, due to their excellent recyclability and eco-friendly nature (Alcock, Cabrera, Barkoula, & Peijs, 2006; Peijs, 2003).

A combination of both trends, i.e. natural fibres and all-polymer composites has recently led to initial work on the development of all-cellulose composites by Nishino and co-workers (Nishino, Matsuda, & Hirao, 2004). In these all-cellulose composites both fibres and matrix are cellulose. Preparation was based on the solubility difference of the cellulose matrix and the reinforcing cellulose fibres in lithium chloride/*N*,*N*-dimethylacetamide (LiCl/DMAc) through pre-treatment. The all-cellulose composites were obtained by dissolving pre-treated cellulose pulp in LiCl/DMAc

---

[*] Corresponding author.
E-mail address: t.peijs@qmul.ac.uk (T. Peijs).

0144-8617/$ - see front matter © 2007 Elsevier Ltd. All rights reserved.
doi:10.1016/j.carbpol.2007.06.019

and then impregnation of the cellulose solution into the aligned ramie fibres followed by coagulation in methanol and drying. These composites showed significant prospect as being a biobased and biodegradable material with excellent mechanical performance. For example, the tensile strength of the created uniaxial all-cellulose composite was 480 MPa which is significantly higher than more traditional random and unidirectional natural fibre reinforced composites (Brahim & Cheikh, 2007; Garkhail et al., 2000; Liu, Misra, Askeland, Drzala, & Mohanty, 2005; Luo & Netravali, 1999; Madsen & Lilholt, 2003; Oksman, Wallstrom, Berglund, & Filho, 2002; Peijs, 2002; Van Den Oever, Bos, & Van Kemenade, 2000).

Ligno-cellulosic fibres, the single component used to prepare this composite, are abundant renewable resources from annual plants, wood, and other agricultural by-products (Gindl & Keckes, 2005). They consist mainly of cellulose, hemi-cellulose, and lignin. In their cell walls, the spirally oriented cellulose plays the role of reinforcements in a soft hemi-cellulose and lignin matrix (Li, Mai, & Ye, 2000). Cellulose is a linear carbohydrate polymer chain consisting of D-glucopyranose units joined together by β-1,4-glycosidic linkages as illustrated in Fig. 1 (Klemm, Schmauder, & Heinze, 2003). In the unit cell of cellulose, two chains are joined by hydrogen bonding to each other in a parallel conformation, which is called cellulose I. These units are packed side-by-side to form microfibrils of cellulose, which also contain disordered or amorphous regions (Edwards, Farwell, & Webster, 1997; Eichhorn & Young, 2004; Gindl & Keckes, 2005). Hemi-cellulose is a highly branched polymer compared to the linearity of cellulose. Its structure contains a variety of sugar units, whereas cellulose contains only 1,4-β-D-glucopyranose units and its degree of polymerization is 10–100 times lower than that of cellulose. Finally, lignin is a complex hydrocarbon polymer with both aliphatic and aromatic constituents (Bledzki & Gassan, 1999; Eichhorn et al., 2001).

The effects of mercerization on the suitability to mechanical treatment, notable tensile strength, of cellulose fibres have been extensively studied. Mercerization or alkali treatment is the process of subjecting a cellulose fibre to an interaction with a relatively concentrated aqueous solution of a strong base, to produce sufficient swelling resulted in a reduction of linear density, shrinkage in dimension and more visible fibrillar structure of a fibre, and change in mechanical properties considerably depend on a treatment time and a concentration of alkali solution. For cellulose fibres, hemi-cellulose has shown to be very sensitive to the action of caustic soda, which exerts only a slight effect on lignin or cellulose (Bledzki & Gassan, 1999; Das, Pal, & Chakraborty, 2006; Gassan & Bledzki, 1999a, 1999b; Ray & Sarkar, 2001; Samal & Ray, 1997; Zhou, Yeung, Yuen, & Zhou, 2004).

In their studies, Samal and Ray (1997) chemically modified pineapple leaf fibres by various techniques and reported that alkali treatment of 4% NaOH solution for 1 h at 35 °C leads to a significant increase in tensile strength when compared to other techniques. A significant enhancement in tensile strength and modulus by 120% and 150%, respectively, of treated jute fibres in 25% NaOH solution for 20 min at 20 °C was revealed in another study by Gassan and Bledzki (1999a, 1999b). Ray and Sarkar (2001) also showed the favourable improvement in tenacity and modulus of jute fibres by 45% and 79%, respectively, after the treatment in 5% NaOH solution for 8 h at 30 °C. For ramie fibres, Zhou et al. (2004) reported a slight increase in tenacity of the treated fibres when only using NaOH solutions of concentrations less than 12% for 10 min treatment at 25 °C.

In the present research, an attempt was made to investigate: (i) the effect of the cellulose solution concentration and its related fibre or matrix volume fraction – on the properties of all-cellulose composites and (ii) the effect of mercerization on the properties of the prepared composites. A variation in fibre volume fraction of the resulting composites can be expected through an impregnation of the cellulose fibres with solutions of different cellulose concentrations as different concentrations will lead to different amounts of cellulose matrix in the final composites. The structure and microstructure of the prepared composites were examined by using scanning electron microscopy, X-ray diffraction, and Raman spectroscopy. Tensile testing was used to characterize the mechanical properties of the composites.

2. Experimental

2.1. Effect of cellulose solution concentration on all-cellulose composite preparation and their properties

2.1.1. Cellulose solution preparation

To prepare cellulose solutions of various cellulose concentrations (1–7% wt/v), a specified amount of ramie fibres (provided from Toyobo Co., Ltd., Japan) were pre-treated by immersing them in distilled water, acetone, and DMAc, each for 24 h at 25 °C and subsequent dissolution in 8% LiCl/DMAc (wt/v) solvent (Dupont, 2003).

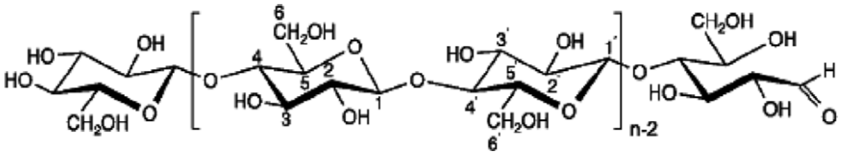


Fig. 1. Molecular structure of cellulose (Edwards et al., 1997).

2.1.2. All-cellulose composite preparation

The as-received ramie fibres were aligned unidirectionally and fixed at both ends in a metal mould as shown in Fig. 2 to prevent shrinkage and distortion. An excess amount of the cellulose solution was applied onto the fibres and then the mould was placed in a vacuum bag system for 2–3 h to achieve sufficient impregnation of the cellulose solution. Subsequently, the mould was taken out of the vacuum bag and an excess of cellulose solution was removed. The moulding was then left at ambient conditions till the cellulose solution started to gel. After 12 h, the fibre-incorporated gel was immersed in methanol to extract DMAc and LiCl from the system. Subsequently, the specimen was dried at room temperature for 12 h, and then in vacuum at 60 °C for 24 h (Nishino et al., 2004).

2.2. Effect of mercerization to properties of the prepared composites

2.2.1. Mercerization of all-cellulose composites

The composites prepared from different concentrations of cellulose solution were treated with 9% NaOH solution for 1 h at room temperature (Gassan & Bledzki, 1999a, 1999b; Ray & Sarkar, 2001; Samal & Ray, 1997; Zhou et al., 2004). The composites were washed with 1% HCl solution to neutralize the remaining alkali, followed by rinsing in distilled water until neutral. After that, the composites were dried in vacuum at 60 °C for 24 h and then further dried at 100 °C for 1 h.

2.3. Characterizations

The structure and morphology of the composites were observed by using a scanning electron microscope (SEM), JEOL JSM 6300 at an accelerating voltage of 10 kV. Prior to examination, a surface of the specimen was coated with a thin layer of gold.

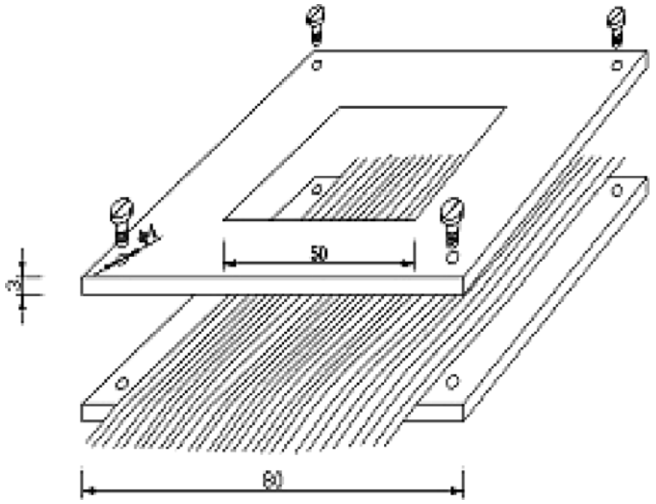


Fig. 2. The aligned ramie fibres fixed within the metal mould.

Tensile testing of the single ramie fibres, the pure matrix, and the composites were performed using an INTRON 5584 tensile tester at room temperature. The initial length of the specimens was 50 mm and the extension rate was 0.5 mm/min. The number of specimens tested was 30 for the single fibres and five for the pure matrix and the composites.

Thermogravimetric (TGA) and differential thermal analyses (DTGA and 2DTGA) data of all-cellulose composites were carried out using a TA Instruments TGA Q500 thermal analyzer. The thermograms were run under nitrogen atmosphere at a heating rate of 50 °C/min using a high-resolution method over a temperature range of 25–800 °C.

The X-ray diffraction profiles of the composites were obtained by using CuKα radiation, generated with X'PERT PRO (Phillips) at 40 kV, 40 mA. The radiation was irradiated perpendicular to the fibre axis of the composites.

To determine orientation of the aligned-fibres in the composites, Raman spectra were examined by using a LABRAM-1B (Dilor). The laser wavelength used was 632.81 nm and the composites were irradiated in both parallel and perpendicular directions to the fibre axis.

Prior to all the measurements, the specimens were conditioned at 100 °C for 1 h and cooled down in desiccators.

3. Results and discussion

With increasing concentration of cellulose in solution the viscosity of these systems increased rapidly as shown in Fig. 3. Such a rapid increase in viscosity will inevitably affect the impregnation process of the fibre bundles resulting in a reduction in cellulose solution uptake into the aligned ramie fibres during impregnation as shown in Fig. 4a. From the two parameters: (i) amount of cellulose solution uptake and (ii) cellulose concentration in solution, the estimated fibre volume fraction of the prepared composites can be determined as illustrated in Fig. 4b. The discussion on these effects to mechanical properties

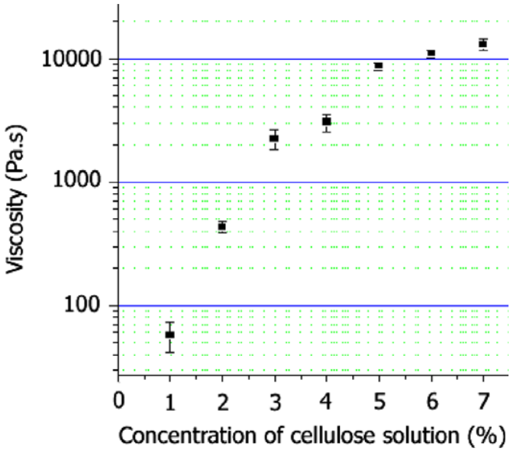


Fig. 3. Effect of cellulose solution concentration on matrix viscosity.

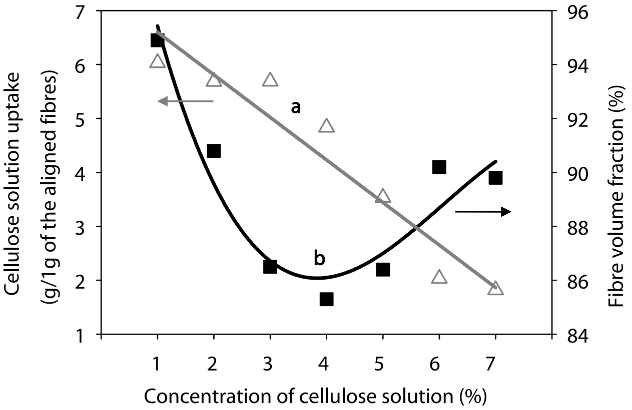


Fig. 4. Effect of cellulose solution concentration to (a) the cellulose solution uptake (g/1 g of aligned-fibres) and (b) fibre volume fraction (%) of the prepared composites.

of the all-cellulose composites in the present work will mainly focus on the change observed in tensile strength. For all the examined specimens, the change in Young's Modulus was rather insignificant and followed no particular trend with moduli in the range of 25 GPa. Fig. 5a plots the tensile strength of all-cellulose composites as a function of different concentrations of cellulose in solution used for the impregnation of each of the composites. With increasing cellulose concentration in solution, an initial increase in tensile strength of the all-cellulose composites is observed up to a level of 4% cellulose solution, while a subsequent reduction in tensile strength is recorded for concentrations above 4%. Interestingly, the optimal cellulose concentration of 4% coincides with the concentration that leads to the lowest fibre volume fraction (~85%) of all prepared composites. At this concentration, the scanning electron micrographs of the composite's cross-sectional view (Fig. 6A) reveals that a sufficient amount of matrix phase and level of impregnation is achieved, which leads to good fibre/matrix adhesion and stress transfer compared to systems based on high (>4%) and low (<4%) cellulose concentrations. For comparison the cross-sections in Fig. 6B and C show the microstructures of the composite prepared with 7% and 1% cellulose concentrations in solution which have approximately 90% and 95% fibre volume fraction, respectively. As revealed in the micrographs, systems based on low (<4%) and high (>4%) cellulose concentrations in solution do not have enough matrix phase for the formation of an optimal composite material. Both these effects, low matrix content due to low cellulose concentrations and poor impregnation of high cellulose concentrations, effectively prevent good stress transfer between the fibres and matrix and leads to inferior properties.

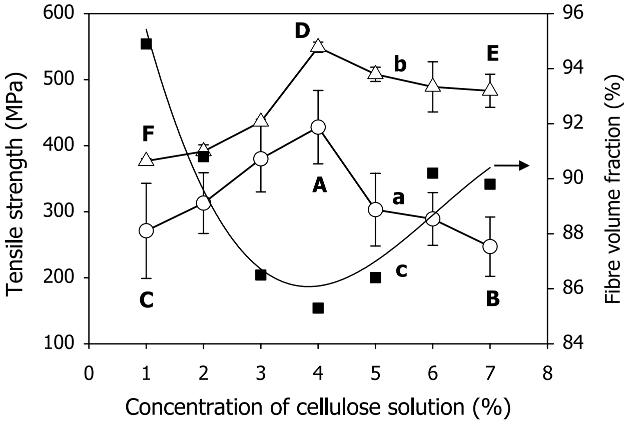


Fig. 5. Effect of cellulose solution concentration to tensile strength of the (a) O un-mercerized and (b) Δ mercerized composites and (c) ■ fibre volume fraction (%) of the prepared composites. (The letters A–F refer to the corresponding micrographs shown in Fig. 6).

Systems based on 3% and 5% cellulose concentration in solution, although having nearly the same fibre volume fraction, show a lower tensile strength for the composite prepared with a 5% concentration compared to the composite prepared with 3% cellulose concentration in solution. This effect is again merely related to poor impregnation and insufficient wet-out of the fibres in the case of composites prepared with high (>4%) cellulose concentrations as a result of high matrix viscosity. Especially, in the case of the 7% cellulose concentration in solution, there is in general poor wet-out of the fibres with some areas having little matrix material while other areas show matrix rich regions. The non-uniform distribution of the matrix throughout these composites results in ineffective load bearing capacity of the ramie fibres and a reduction in performance.

Next to the effect of cellulose solution concentration the effect of mercerization was studied. After mercerization, an enhancement of 15–95% in tensile strength of composites prepared with 1–7% cellulose concentration in solution was obtained (see Fig. 5b). As expected, the composite prepared with 4% cellulose concentration still exhibits the best mechanical performance. For this particular composite, the properties are nearly comparable to that of a single ramie fibre, demonstrating the high efficiency of the fibres in this composite as illustrated in Fig. 7.

During mercerization, the alkali solution penetrates through the composites and hemi-celluloses, which are very sensitive to the action of this solution, are removed (Bledzki & Gassan, 1999; Gassan & Bledzki, 1999a, 1999b; Ray & Sarkar, 2001; Samal & Ray, 1997). From the thermogravimetry (TGA), derivative thermogravimetry (DTGA), and second derivative thermogravimetry (2DTGA) curves, the un-mercerized composite prepared with 4% cellulose concentration in solution (Fig. 8a) shows two decomposition steps after an initial loss of moisture between 60 and 100 °C. The first decomposition peak at 313 °C is due to the hemi-cellulose degradation (14% weight loss; Table 1) and the second decomposition peak at about 323 °C is caused by the α-cellulose degradation (57% weight loss). However, in the mercerized composites (Fig. 8b), the thermograms exhibit only one decomposition peak at 305 °C with 58% weight loss. The missing peak for hemi-cellulose decomposition in the mercerized composite indicates that

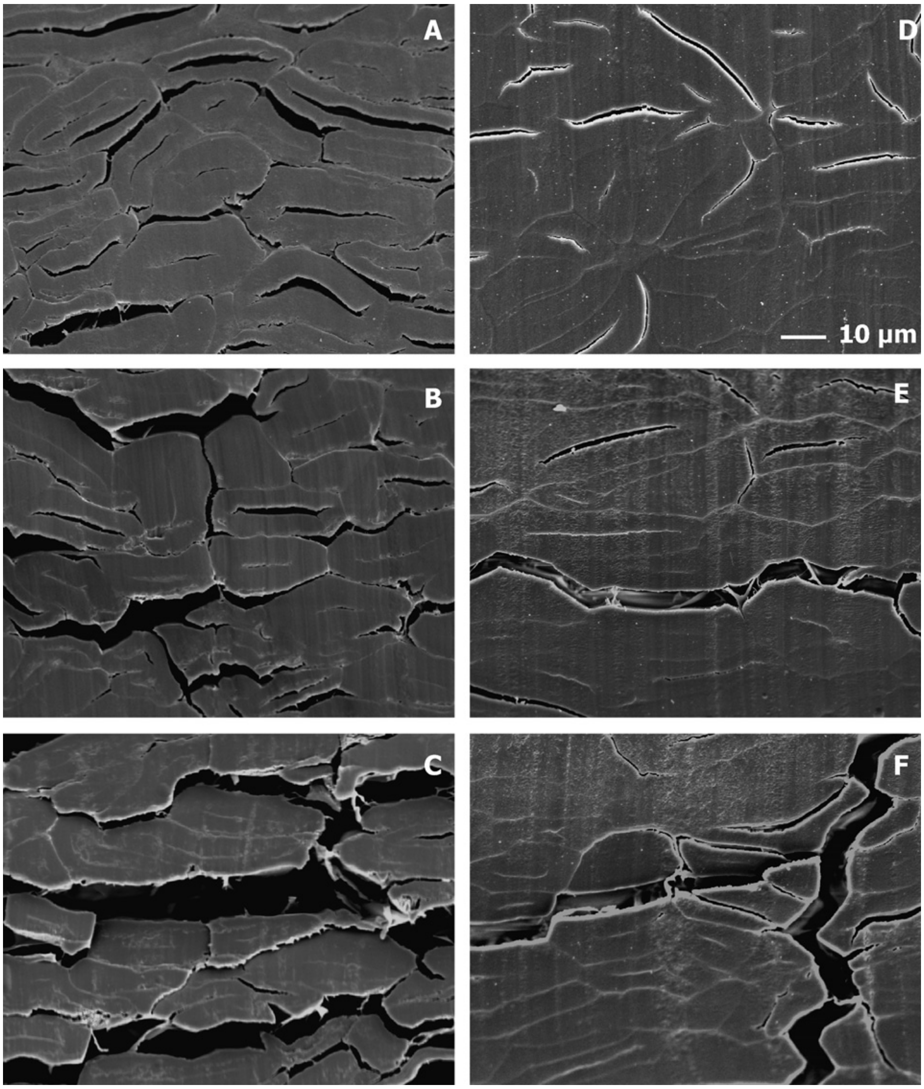


Fig. 6. Scanning electron micrographs of cross-sectional view of the un-mercerized prepared with 4% (A), 7% (B), and 1% (C) cellulose concentrations in solution which have 0.85, 0.90, and 0.95 fibre volume fraction, respectively, and the mercerized composites prepared with 4% (D), 7% (E), and 1% (F) cellulose concentrations in solution.

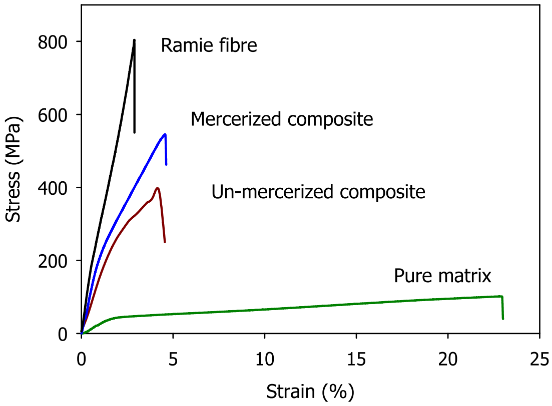


Fig. 7. Stress–strain curves of the ramie fibre, un- and mercerized composites prepared with 4% cellulose solution, and the pure matrix.

approximately 14% weight of hemi-cellulose is removed from the un-mercerized composite due to the mercerization. Furthermore, a lowering of the degradation temperature and an increase in residue char formation of mercerized composite can infer to their inferior thermal stability compared to the un-mercerized composite (Albano, Gonzalez, Ichazo, & Kaiser, 1999; Jandura, Riedl, & Kokta, 2000; Nada & Hassan, 2000; Ray, Sarkar, Basak, & Rana, 2002).

After removal of hemi-cellulose during mercerization of ligno-cellulosic fibres, it has been proposed by other researchers that this causes the inter-fibrillar regions in ligno-cellulosic fibres to become less dense and rigid, thereby allowing the cellulose microfibrils to rearrange themselves for better chain orientation and packing including the highly distorted crystalline and amorphous regions which can lead to an increase in fibre strength (Bledzki & Gassan, 1999; Gassan & Bledzki, 1999a, 1999b; Ray & Sarkar, 2001; Sao, Samantaray, & Bhattacherjee, 1996). In the present study, however, we did not just treat the fibres but the whole composites. Therefore, it is believed that during mercerization a swelling of the composites leads to a

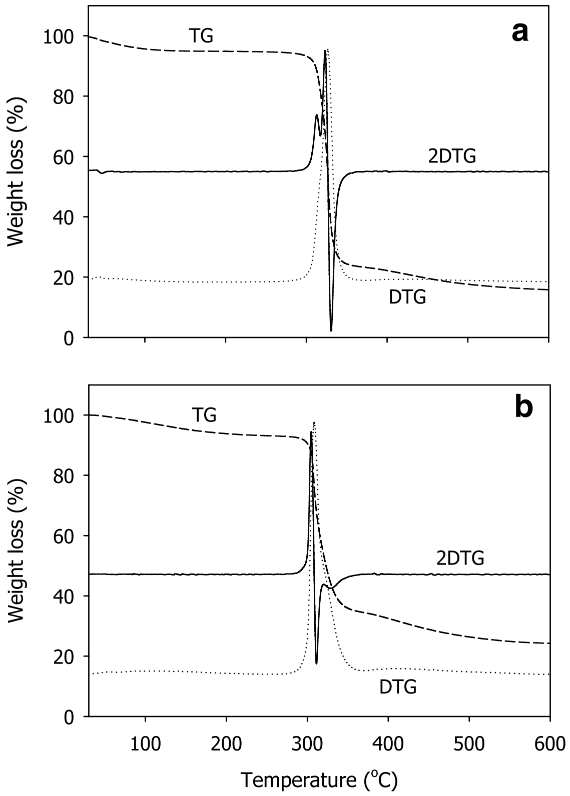


Fig. 8. Thermogravimetric analyses of the (a) un- and (b) mercerized composites prepared with 4% cellulose solution.

Table 1
Results of thermogravimetric analysis of the un- and mercerized composites prepared with 4% cellulose solution

Composite samples	Peak temperature (°C)	% Degradation	% Residue at 600 °C
Un-mercerized	312.9	14.2	15.8
	323.2	57.3	
Mercerized	304.8	58.2	24.3

healing of cracks and voids between the reinforcing fibres and merges them together which results in a greatly improved interface in the treated composites as revealed in Fig. 6 is a main reason for their enhanced mechanical properties (see Fig. 5b). After mercerization, better interfacial properties of the mercerized composites (Figs. 6D–F), thinner interfacial matrix regions and less voids as compared to the un-mercerized composite (Figs. 6A–C) are observed. Moreover, the mercerized composites show a better optical transparency (Fig. 9) which is another indication for improved interfacial interaction as less light is scattered at their interfaces.

As mentioned earlier, for un-mercerized composites, a high viscosity of impregnating solutions caused an insufficient wet-out of the fibres leading to a poor matrix distribution throughout composites, therefore, the composites prepared with high (>4%) cellulose concentrations in solution show lower strengths compared to the composites prepared with low (<4%) cellulose concentrations in solution (Fig. 5a). Interestingly, the alkali treated composites prepared with high (>4%) cellulose concentrations in solution conversely show higher strengths with a markedly enhancement of 67% up to 95%, whereas the treated composites prepared with low (<4%) concentrations gain only 15–38% enhancement in their strength (see Fig. 5a and b). In case of mercerization, an insufficient wet-out of the fibres in their corresponding untreated composites seems to become beneficial to the alkali treatment and leads to greater enhancements and higher strengths of the treated composites. Further investigation should be carried out to clarify the true enhancement mechanism in the composite after mercerization.

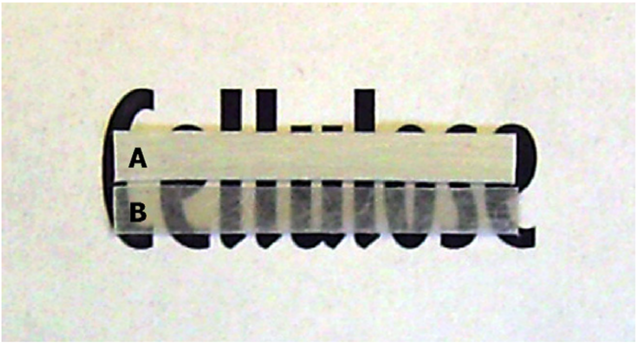


Fig. 9. Optical photograph of the (A) un-mercerized and (B) mercerized composites prepared with 4% cellulose solution.

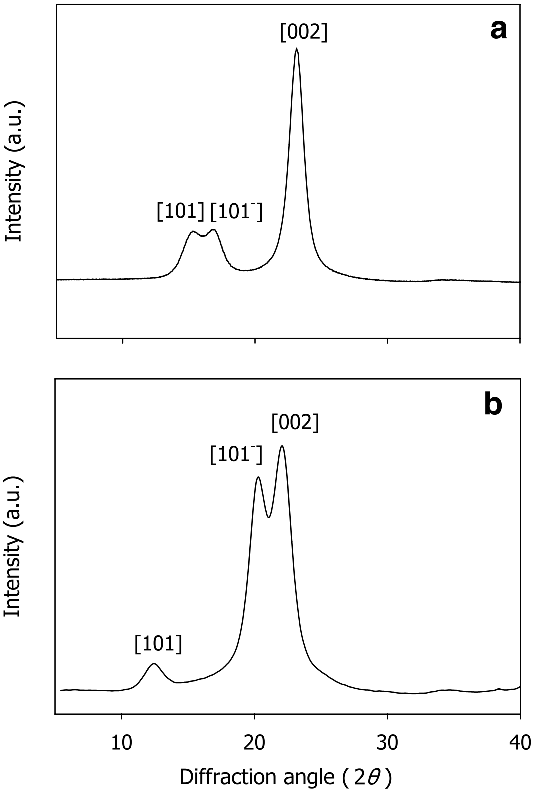
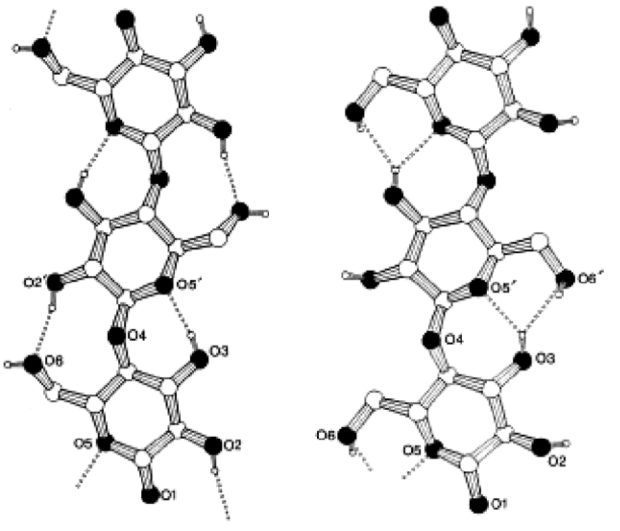


Fig. 10. X-ray diffraction profiles of the (a) un-mercerized and (b) mercerized composites prepared with 4% cellulose solution.

During mercerization, swelling of native cellulosic materials in the alkali solution, which is the main polymorphic modification of cellulose in the composites, causes a rearrangement of the crystal packing of chains from native cellulose I (chains aligned in a parallel conformation) to cellulose II (an anti-parallel conformation) (Ass, Belgacem, & Frollini, 2006; Jähn, Schröder, Füting, Schenzel, & Diepenbrock, 2002; Sao et al., 1996). In Fig. 10a, the X-ray diffraction spectrum of the un-mercerized composite shows some similarity to that of the ramie fibres, which exhibits an intense sharp reflection at $2\theta = 23°$ and two overlapping weaker diffractions at $2\theta = 15°$ and 17° that are assigned to the $[0\,0\,2]$, $[1\,0\,1]$, and $[1\,0\,1^{-}]$ lattice planes of cellulose I (Edwards et al., 1997). After mercerization, the composite shows the characteristic diffraction pattern of cellulose II (Fig. 10b) as indicated by the appearance of diffractions at $2\theta = 22°$, 12°, and 20° resulting from the $[0\,0\,2]$, $[1\,0\,1]$, and $[1\,0\,1^{-}]$ lattice planes of cellulose II (Zhou et al., 2004). The significant increase in mechanical properties of the mercerized composites are even more surprising in light of the transition from cellulose I to cellulose II as cellulose II generally displays a lower chain modulus. This is due to the two different conformations of the hydroxymethyl group that will cause variations in intra-molecular hydrogen bonding as shown in Fig. 11. The modulus of the cellulose I chain is around 140 GPa, while that of cellulose II is 90 GPa (Northolt et al., 2001). These have important consequences for the ultimate tensile properties of the fibres which generally would imply inferior reinforcing capabilities for cellulose II based composites. However, as shown in Fig. 5, in our case the mercerized (cellulose II) composites exhibited better mechanical properties than the un-mercerized composites that have cellulose I (native cellulose fibres) as reinforcement. The enhancement is therefore presumably more related to a better efficiency of the ramie fibres in the composite due to the improvement in interfacial properties of the mercerized composites as revealed by the scanning electron micrographs (Fig. 6) rather than due to conformational changes in the cellulose structure.



Cellulose I
Cellulose II

Fig. 11. The chain conformations of cellulose I and cellulose II (Northolt et al., 2001).

The remaining high level of molecular orientation of the aligned ramie fibres in the mercerized composites as revealed by FT-Raman spectra (Fig. 12) is another indication for the high performance of these composites. Fig. 12 compares the spectra of the aligned ramie fibres (Fig. 12a), with both un- and mercerized composites (Fig. 12b and c, respectively). In the case of both types of all-cellulose composites, glycosidic linkages of cellulose (C–O–C), which represent the backbone of the polymer chains (Fig. 1), show more intense Raman signals of the ν_s(C–O–C) mode with parallel polarization. Also the methine groups (CH) of the glucopyranose units which are mainly oriented perpendicular to the backbone of the cellulose chains show more intense Raman signals of the ν(CH) mode with perpendicular polarization for the composites. These large differences

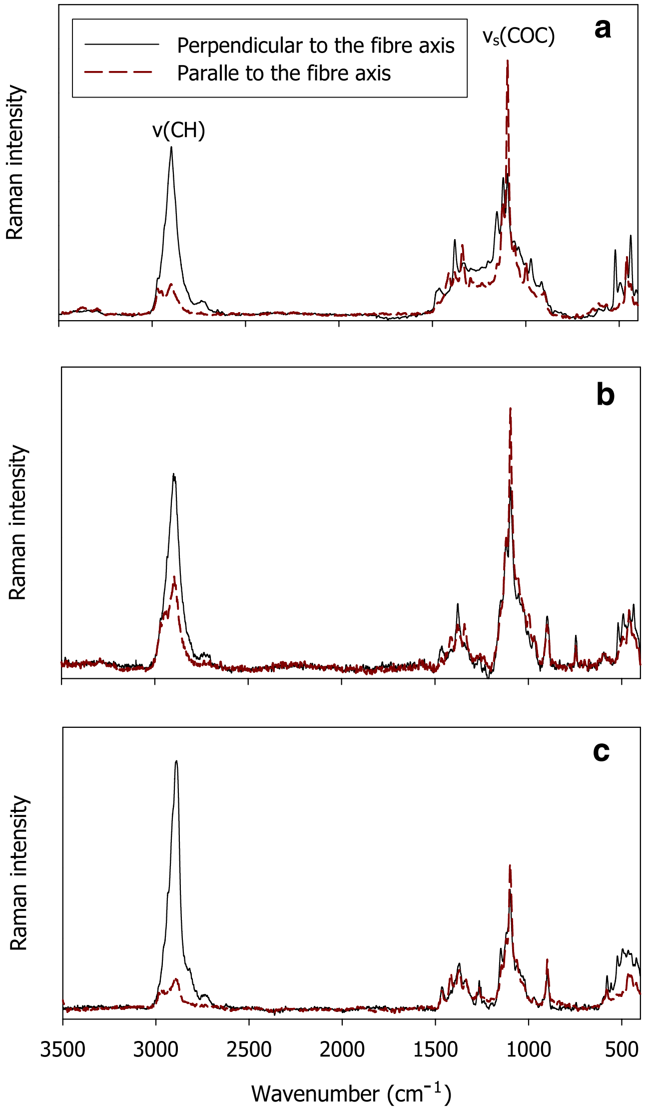


Fig. 12. Raman spectra of (a) ramie fibres, (b) un-mercerized, and (c) mercerized composites prepared with 4% cellulose solution.

between perpendicular and parallel polarized spectra suggest that, in both un-mercerized and mercerized composites, the backbone of the cellulose chains tend to be predominantly aligned parallel to the fibre axes and that molecular orientation is well-maintained in the reinforcing fibres (Cao, Shen, Lu, & Huang, 2006; Fischer, Schenzel, Fischer, & Diepenbrock, 2005; Jähn et al., 2002). The differences in the spectra characteristics of the un- and mercerized composites are supposedly caused by a change from cellulose I to cellulose II conformation of cellulose in the composites after mercerization (Ass et al., 2006; Fischer et al., 2005; Jähn et al., 2002).

In order to evaluate the current all-cellulose composites, the tensile strength of these composites was compared to the other random (2D, in-plane isotropic) and unidirectional (UD) natural fibre reinforced composites (Brahim & Cheikh, 2007; Garkhail et al., 2000; Liu et al., 2005; Luo & Netravali, 1999; Madsen & Lilholt, 2003; Oksman et al., 2002; Van Den Oever et al., 2000). As shown in Fig. 13 the mechanical properties of the current all-cellulose composites with strengths up to 540 MPa after mercerization compare very favourably to other composites. This is undoubtedly due to their high fibre volume fraction, good fibre orientation, and good interfacial properties. For better quantitative analyses of the data, the fibre efficiency factor for strength of the composites was calculated using the well known "rule of mixtures" modified by Cox-Krenchel:

$$\sigma_c = \eta_f \eta_0 [V_f \sigma_f + V_m \sigma_m] \tag{1}$$

where σ_c is the strength of the composites, η_f is the fibre efficiency factor for composite strength considering stress transfer from the matrix to the fibres, η_0 is the fibre orientation factor ($\eta_0 = 1$ for a UD composite and $\eta_0 = 3/8$ for a 2D (in-plane) composite), σ_f is the strength of fibres, V_f is the volume fraction of fibre, σ_m is the strength of matrix, V_m is the volume fraction of matrix (Garkhail et al., 2000; Oksman et al., 2002; Van Den Oever et al., 2000). Table 2 lists the tensile properties of the as-received ramie fibres and pure cellulose matrix used for calculations of the fibre efficiency factor of the composites.

As illustrated in Fig. 14, the fibre efficiency factor of the un-mercerized composites are in the same range, around 0.4–0.6, as 2D (in-plane) random natural fibre reinforced polypropylene composites, both without (2D) and with maleic anhydride compatibilizer (2D + C), whereas the mercerized composites with improved interfacial properties are more comparable to the UD composites of previous works of Luo et al. (UD-2) and Oksman et al. (UD-3), showing a high efficiency of up to 82% of the fibre strength. The fibre efficiency factor of the composites in Madsen et al. work (UD-1) could not be calculated because of absence of fibre property data.

Compared to the initial work of Nishino et al. (2004), the all-cellulose composite prepared with 3% cellulose con-

Table 2
The properties of the as-receive ramie fibres and pure cellulose (ramie) matrix (standard deviation in parentheses)

Tensile properties	Ramie fibres	Pure matrix
Tensile strength (MPa)	768.4 (154)	101.6 (20)
Young's modulus (GPa)	42.0 (8)	2.5 (0.6)
Elongation at max load (%)	2.6 (0.7)	20.6 (5.7)

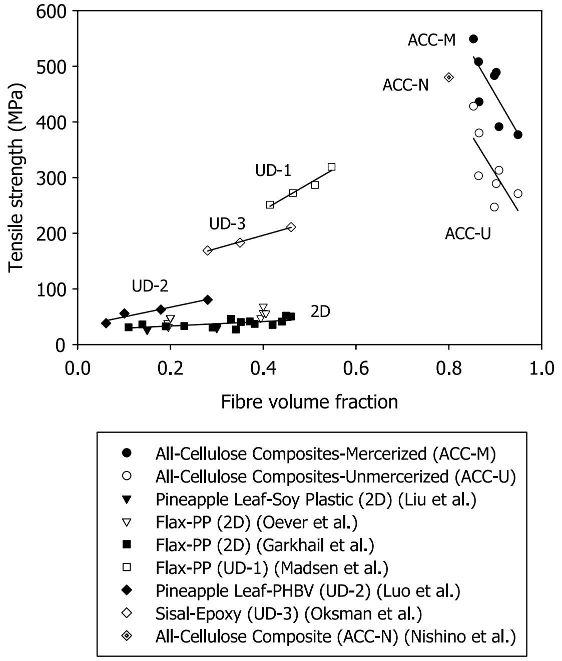


Fig. 13. Comparison of tensile strength of the all-cellulose composites to other random (2D) and unidirectional (UD) natural fibres based composites.

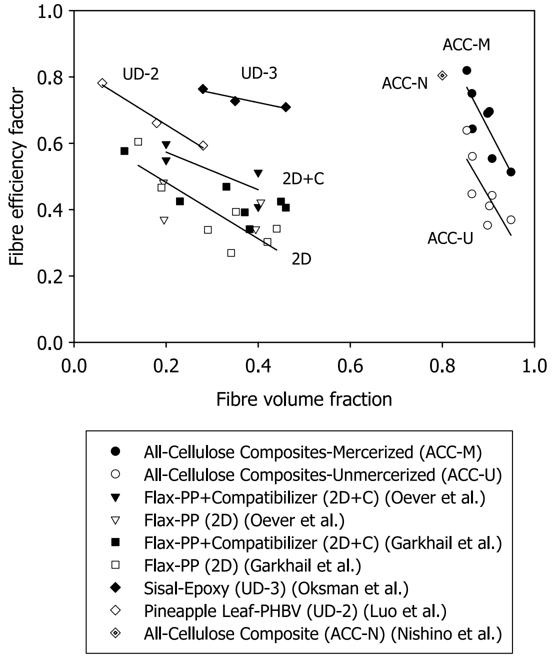


Fig. 14. Comparison of fibre efficiency factor of the all-cellulose composites to other random (2D) and unidirectional (UD) natural fibres based composites.

centration in solution resulted in a fibre volume fraction of 0.80, whereas the composite prepared with the same concentration in this present work resulted in a fibre volume fraction of 0.86. However, the all-cellulose composite of Nishino et al. (2004) exhibits a slightly higher tensile strength and especially, fibre efficiency factor when compared to the current un-mercerized composites (see Figs. 13 and 14). These different outcomes are believed to be caused by the differences in raw materials and preparation techniques between both works. The current mercerized composites on the other hand exhibit the highest tensile strength and fibre efficiency of all the all-cellulose composites.

4. Conclusions

All-cellulose composites with 85% up to 95% fibre volume fraction were prepared by using 1–7% cellulose concentrations in solution for impregnation of ligno-cellulosic ramie fibres. Tensile strength of the all-cellulose composites increased with cellulose concentration up to a concentration level of 4%, while a reduction in tensile strength is observed for concentrations above 4%. High cellulose concentrations (>4%), results in a high viscosity of the matrix solution and a poor impregnation and wet-out of the fibres. Composites prepared with the 4% cellulose concentration, having the lowest fibre volume fraction of around 85%, exhibited the highest tensile strength. For these conditions, the composite has a sufficient amount of matrix phase, good wetting and interfacial interaction between fibres and matrix, resulting in highly efficient all-cellulose composites. In addition to the effect of cellulose concentration in solution the effect of mercerization of the all-cellulose composites was investigated. It was shown that mercerization causes a significant improvement (up to 95%) in tensile strength of the treated composites. The origin for these enhanced properties is thought to be related to a better efficiency of the ramie fibres in the composite due to an improvement in interfacial properties for the mercerized all-cellulose composites as revealed by the scanning electron micrographs. The mechanical properties of the all-cellulose composites with strengths up to 540 MPa for mercerized composites compare very favourable with other more traditional natural fibre based composites, mainly due to their high fibre volume fraction and good interfacial properties. Raman spectroscopy indicated that the molecular orientation of the cellulose fibres in the mercerized composites was well-maintained. However, after mercerization, native cellulose I, which is the major polymorphic modification of cellulose in the composites, is rearranged to cellulose II crystal packing.

Acknowledgements

Financial supports from the Asia-link program Grant Number ASI/B7-301/98/679-32 (CQ) and the Royal Thai Government (NS) are gratefully acknowledged. Ramie fibres were kindly supplied by Toyobo Co., Ltd., Japan. The authors wish to thank to Prof. T. Nishino, N. Stingelin-Stutzmann, and C. Reynolds for general discussions, M. Philips for material characterization discussions, R. Smith for discussions on Raman spectroscopy, Z. Luklinska, and M. Willis for SEM assistance and K. Berketis and S. Savona for mechanical testing assistance.

References

Albano, C., Gonzalez, J., Ichazo, M., & Kaiser, D. (1999). Thermal stability of blends of polyolefins and sisal fiber. *Polymer Degradation and Stability, 66*, 179–190.

Alcock, B., Cabrera, N. O., Barkoula, N.-M., & Peijs, T. (2006). The mechanical properties of unidirectional all-polypropylene composites. *Composites, Part A, 37*(5), 716–726.

Ass, B. A. P., Belgacem, M. N., & Frollini, E. (2006). Mercerized linters cellulose: Characterization and acetylation in *N*,*N*-dimethylacetamide/lithium chloride. *Carbohydrate Polymers, 63*, 19–29.

Bledzki, A. K., & Gassan, J. (1999). Composites reinforced with cellulose based fibres. *Progress in Polymer Science, 24*, 221–274.

Brahim, S. M., & Cheikh, R. B. (2007). Influence of fibre orientation and volume fraction on the tensile properties of unidirectional Alfa-polyester composite. *Composites Science and Technology, 67*, 140–147.

Cao, Y., Shen, D., Lu, Y., & Huang, Y. (2006). A Raman-scattering study on the net orientation of biomacromolecules in the outer epidermal walls of mature wheat stems (*Triticum aestivum*). *Annals of Botany, 97*, 1091–1094.

Das, M., Pal, A., & Chakraborty, D. (2006). Effects of mercerization of bamboo strips on mechanical properties of unidirectional bamboo novolac composites. *Journal of Applied Polymer Science, 100*, 238–244.

Dupont, A.-L. (2003). Cellulose in lithium chloride/*N*,*N*-dimethylacetamide, optimisation of a dissolution method using paper substrates and stability of the solutions. *Polymer, 44*, 4117–4126.

Edwards, H. G. M., Farwell, D. W., & Webster, D. (1997). FT Raman microscopy of untreated natural plant fibres. *Spectrochimica Acta Part A, 53*, 2383–2392.

Eichhorn, S. J., Baillie, C. A., Zafeiropoulos, N., Mwaikambo, L. Y., Ansell, M. P., Dufresne, A., et al. (2001). Review: Current international research into cellulosic fibres and composites. *Journal of Materials Science, 36*, 2107–2131.

Eichhorn, S. J., & Young, R. J. (2004). Composite micromechanics of hemp fibres and epoxy resin microdroplets. *Composites Science and Technology, 64*, 767–772.

Fischer, S., Schenzel, K., Fischer, K., & Diepenbrock, W. (2005). Applications of FT Raman spectroscopy and micro spectroscopy characterizing cellulose and cellulosic biomaterials. *Macromolecules Symposium, 223*, 41–56.

Gassan, J., & Bledzki, A. K. (1999a). Alkali treatment of jute fibres: Relationship between structure and mechanical properties. *Journal of Applied Polymer Science, 71*, 623–629.

Gassan, J., & Bledzki, A. K. (1999b). Possibilities for improving the mechanical properties of jute/epoxy composites by alkali treatment of fibres. *Composite Science and Technology, 59*, 1303–1309.

Garkhail, S. K., Heijenrath, R. W. H., & Peijs, T. (2000). Mechanical properties of natural-fibre-mat-reinforced thermoplastics based on flax fibres and polypropylene. *Applied Composite Materials, 7*(5–6), 351–372.

Gindl, W., & Keckes, J. (2005). All-cellulose nanocomposite. *Polymer, 46*, 10221–10225.

Jähn, A., Schröder, M. W., Füting, M., Schenzel, K., & Diepenbrock, W. (2002). Characterization of alkali treated flax fibres by means of FT Raman spectroscopy and environmental scanning electron microscopy. *Spectrochimica Acta Part A, 58*, 2271–2279.

Jandura, P., Riedl, B., & Kokta, B. V. (2000). Thermal degradation behavior of cellulose fibers partially esterified with some long chain organic acids. *Polymer Degradation and Stability, 2000*, 387–394.

Klemm, D., Schmauder, H., & Heinze, T. (2003). *Cellulose* (1st ed.). *Biopolymers* (Vol. 6). Weinheim: Wiley-VCH, 275–285.

Li, Y., Mai, Y.-W., & Ye, L. (2000). Sisal fibre and its composites: A review of recent developments. *Composite Science and Technology, 60*, 2037–2055.

Liu, W., Misra, M., Askeland, P., Drzala, L. T., & Mohanty, A. K. (2005). 'Green' composites from soy based plastic and pineapple leaf fiber: Fabrication and properties evaluation. *Polymer, 46*, 2710–2721.

Luo, S., & Netravali, A. N. (1999). Mechanical and thermal properties of environment-friendly "green" composites made from pineapple leaf fibers and poly(hydroxybutyrate-co-valerate) resin. *Polymer Composites, 20*, 367–378.

Madsen, B., & Lilholt, H. (2003). Physical and mechanical properties of unidirectional plant fibre composites – an evaluation of the influence of porosity. *Composites Science and Technology, 63*, 1265–1272.

Nada, A. M. A., & Hassan, M. L. (2000). Thermal behavior of cellulose and some cellulose derivatives. *Polymer Degradation and Stability, 67*, 111–115.

Nishino, T., Matsuda, I., & Hirao, K. (2004). All-cellulose composite. *Macromolecules, 37*, 7683–7687.

Northolt, M. G., Boerstoel, H., Maatman, H., Huisman, R., Veurink, J., & Elzerman, H. (2001). The structure and properties of cellulose fibres spun from an anisotropy phosphoric acid solution. *Polymer, 42*, 8249–8264.

Oksman, K., Wallstrom, L., Berglund, L. A., & Filho, R. D. T. (2002). Morphology and mechanical properties of unidirectional sisal–epoxy composites. *Journal of Applied Polymer Science, 84*, 2358–2365.

Peijs, T. (2002). Composites turn green. *e-Polymers, n. T_002*, 1–12.

Peijs, T. (2003). Composites for recyclability. *Materials Today, April*, 30–35.

Ray, D., & Sarkar, B. K. (2001). Characterization of alkali-treated jute fibres for physical and mechanical properties. *Journal of Applied Polymer Science, 80*, 1013–1020.

Ray, D., Sarkar, B. K., Basak, R. K., & Rana, A. K. (2002). Study of the thermal behavior of alkali-treated jute fibers. *Journal of Applied Polymer Science, 85*, 2594–2599.

Samal, R. K., & Ray, M. C. (1997). Effect of chemical modifications on FTIR spectra. II. Physicochemical behavior of pineapple leaf fibre (PALF). *Journal of Applied Polymer Science, 64*, 2119–2125.

Sao, K. P., Samantaray, B. K., & Bhattacherjee, S. (1996). X-ray line profile analysis in alkali-treated ramie fibre. *Journal of Applied Polymer Science, 60*, 919–922.

Van Den Oever, M. J. A., Bos, H. L., & Van Kemenade, M. J. J. M. (2000). Influence of the physical structure of flax fibres on the mechanical properties of flax fibre reinforced polypropylene composites. *Applied Composite Materials, 7*, 387–402.

Zhou, L. M., Yeung, K. W., Yuen, C. W. M., & Zhou, X. (2004). Characterization of ramie yarn treated with sodium hydroxide and crosslinked by 1,2,3,4-butanetetracarboxylic acid. *Journal of Applied Polymer Science, 91*, 1857–1864.