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All-Cellulose Composites by Surface Selective Dissolution

of Aligned Ligno-Cellulosic Fibres

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Abstract

All-cellulose composites were successfully prepared by a surface selective dissolution method of aligned ligno-cellulosic fibres using lithium chloride/*N,N*-dimethylacetamide as a solvent. The effect of the immersion time of the aligned fibres in the solvent during preparation was investigated. The structure and mechanical properties of the composites were characterized by X-ray diffraction, scanning electron microscopy, and tensile testing. Optimization of the immersion time resulted in all-cellulose composites with excellent mechanical properties, i.e. a longitudinal tensile strength and Young's modulus of 460 MPa and 28 GPa, respectively. Strong interfacial interaction was also observed for these all-cellulose composites with good interface dominated properties like transverse tensile strengths in the range of 22-40 MPa. The significant advantages of these composites are their biobased and biodegradable character combined with excellent mechanical properties due to their very high fibre

volume fraction which makes them as a potential alternative to glass-fibre-reinforced composites.

1. Introduction

Nowadays, the growing environmental awareness throughout the world has triggered a paradigm shift towards designing environmentally friendly materials. Consequently, in recent years, natural fibres have attracted more and more interest as reinforcements for both thermoplastic and thermosetting polymer composites [1-6]. However, most of the commercially available polymers used as composite matrices are currently petroleum-based, non-biodegradable and regarded as non-sustainable materials [7-10]. On the other hand, current biobased composites based on biodegradable polymers are often of modest strength and not cost-effective at present [10-16]. Moreover, for composites which are generally composed of two chemically foreign components, a strong interfacial interaction between fibre and matrix is required to obtain efficient reinforcement because only a well formed interface allows good stress transfer from matrix to fibre. In case of using natural fibres as reinforcement, an improvement in fibre-matrix adhesion is usually achieved by fibre surface- or matrix modifications, addition of compatibilizers or coupling agents or using other techniques at the expense of increased processing cost and time [17-20].

The most desirable solution to all these problems is possibly the idea of self-reinforced composites such as the all-polypropylene composites [21-24], which have recently been developed. These composites are basically monomaterials and therefore fully recyclable and environmentally friendly. Moreover, since both fibre and matrix are

composed of the same material they show excellent interfacial compatibility. Next to more traditional ways of creating all-polymer composites through the impregnation of polymer fibres with a polymer matrix of a slightly lower melting temperature, recently two more innovative routes have been proposed for the manufacture of all-polymer composites. First, the 'hot compaction' process was developed at the University of Leeds [21-22], which is based on the selective melting of the fibre surface and subsequently 'welding' fibres together rather than impregnating them with polymer matrix. In this approach part of the highly oriented polymer fibre is melted and upon cooling under pressure, the molten fibre material recrystallises into a matrix, which bonds the fibres together and forms a perfect interface [21-22]. In order to overcome the extremely small processing temperature window which is needed to transform the optimum amount of fibre material into matrix material an alternative route was proposed by Peijs and co-workers [23-24], which is based on the consolidation of co-extruded fibres. In this method a high modulus polypropylene homopolymer tape (read: fibres) is co-extruded with a thin coating of a lower melting temperature copolymer (read: matrix). The resulting all-polypropylene composites have a large processing window and their exceptionally high fibre volume fraction of around 90% makes them highly competitive with conventional glass-fibre-reinforced composites of much lower fibre loadings in various potential applications particularly the automotive industry.

Following on the successes of all-polymer composites like all-PP [21-24], all-cellulose composites have recently been introduced [25-26]. In a similar fashion to all-polymer composites an approach can be followed where cellulose fibres are impregnated with a cellulose matrix. Such an approach was followed for the creation of high-strength all-cellulose composites where ramie fibres are the reinforcement and

dissolved Kraft pulp [25] or dissolved ramie fibre [26] is used for the matrix. Due to the high fibre volume fraction in these composites, the tensile strength of these uniaxially reinforced all-cellulose composites was as high as 480-540 MPa which compared very favourably to other nature fibre based composites. The all-cellulose composites described were obtained by dissolving pre-treated cellulose fibres in lithium chloride/*N,N*-dimethylacetamide (LiCl/DMAc) and then impregnation of the cellulose solution into the aligned ramie fibres followed by coagulation in methanol and drying.

Ligno-cellulosic or natural fibres from annual plants, wood, and agricultural by-products is an abundant renewable resource [27]. Ramie fibre was selected for this study because of its excellent fibre characteristics. Ramie or china grass (*Boehmeria nivea* (L.) Gaud.) is a perennial herbaceous plant of the Urticaceous family. Ramie fibres are strong, very fine and silk-like, naturally white in colour, and have a high lustre. Other advantages are its good resistance to bacterial, mildew, and insect attack. Furthermore, the fibres are stable in alkaline media and not harmed by mild acids [14]. Due to the excellent fibre properties previously mentioned, ramie fibres have, therefore, a high potential as a raw material for preparing high performance cellulose based composites.

As mentioned earlier, one potential route to the creation of all-cellulose composites is through a traditional impregnation method. However, similar to other composite systems the impregnation of fibre bundles with high viscosity polymer systems has always been a difficulty. Another technique to prepare all-cellulose based composites has also been previously proposed by Matsumura *et al.* and Lu *et al.* [8,28]. In these works, wood pulp and sisal fibres were partially converted to the thermoplastic cellulose esters which were afterwards thermally consolidated into a continuous matrix reinforced with the remained (unsubstituted) cellulose. The various extent of chemical

modification influences a melt processability and reinforcing effect of these composites. The present study focuses on an alternative approach for the preparation of all-cellulose composite. Rather than impregnating cellulose fibres with a highly viscous cellulose matrix or chemically modifying cellulose fibres as were reported previously [8,25-26,28], here surface selective dissolution of aligned cellulose fibres in the solvent by controlling the immersion time was employed. A similar approach has been used previously to prepare random all-cellulose composites from filter paper by Nishino *et al.* [29]. As the cell wall of a natural fibre is made up of a number of layers, the surface layer of the fibres can be partially dissolved and transformed into the matrix phase of the composites. Meanwhile, the remaining fibre cell cores maintain their original structure and impart a reinforcing effect to the composite [8,30-31]. This approach is similar to the 'selective melting' approach for self-reinforced composites where the fibre skin is also transformed into a matrix phase but now through melting [21-24]. Clearly, in the case of cellulose where melting is not an option the matrix phase needs to be created through a surface selective dissolution process rather than melting as illustrated in Figure 1. The effect of immersion time of the aligned fibres in the solvent during preparation, which is the determining step of how much of the outer layer of the fibres is dissolved to form a matrix phase, was investigated in this study. With increasing immersion time, larger fractions of fibre can be dissolved to form a matrix phase, leading to composites of different fibre volume fractions. Since both the fibre and matrix phases of this cellulose composite are of the same origin and hence are chemically identical, a strong interfacial adhesion can be expected between them [12,24]. The structure of the all-cellulose composites was examined by X-ray diffraction

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and scanning electron microscopy. Tensile testing was used to characterize the mechanical properties of the prepared all-cellulose composites.

2. Experimental details

2.1 Sample preparation

Ramie fibres, kindly supplied by Toyobo Co., Ltd., Japan were aligned in the longitudinal direction and were then fixed at both ends in a metal mould (dimension 50 × 50 mm) to prevent shrinkage and distortion. Table 1 summarizes the characteristic information of the as-received ramie fibres. The activation of the fibres was performed by immersing the fibres in distilled water, acetone, and DMAc, respectively, each for 2 hours at room temperature. Then, the activated fibres (0.36% wt/v) were immersed in 8% wt/v LiCl/DMAc solvent for a specified immersion time of 1, 2, 3, 4, 5, 6, 9, and 12 hours. The fibres were then removed from the solvent and the partially dissolved fibres started to gel by exposing them to ambient conditions for 12 hours. Subsequently, this fibre-incorporated gel was immersed in methanol for 12 hours to extract the DMAc and LiCl from the system. During this step, the methanol was exchanged by fresh methanol repeatedly after 1 hour and 6 hours of the immersion. Next the specimens were dried at room temperature for 12 hours, and then further under vacuum at 60 °C for 24 hours.

2.2 Measurements

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

X-ray diffraction profiles were detected using Cu Kα radiation, generated with RINT-2000 (Rigaku Co.) at 40 kV, 20 mA. The X-ray beam was operated in reflection

mode and irradiated on the specimen perpendicular to the fibre orientation. After subtracting the air scattering, the diffraction profile was curve resolved into non-crystalline (amorphous) scattering and crystalline reflections using Rigaku multi-peaks separation software, whereby the amorphous contribution was estimated from the fully dissolved/regenerated cellulose matrix profile. The apparent crystallinity (%) was determined from the ratio of their area [29]. X-ray diffraction photographs were taken with a flat camera with a camera length of 37.5 mm.

Mechanical properties of the composites were assessed with a universal tensile tester, Instron 5584, at room temperature. The gauge length of the specimens with a width of 3 mm was 20 mm and a cross-head speed of 20 mm/min was utilized for the tests similar to Nishino *et al.* [25] which previously prepared all-cellulose composites by an impregnation method. Elongation at break, ultimate tensile strength, and Young's modulus of the composites were evaluated. The results were reported as the average value of at least five measurements.

Prior to all measurements, the specimens were conditioned at a controlled relative humidity of 55.9 ± 0.3 % at 15 °C (according to ASTM E104).

3. Results and discussion

Comparison of the X-ray diffraction patterns of all-cellulose composites (Figure 2) shows that the crystallinity of the composites decreased with the immersion time of the ramie fibres in the solvent. Without doubt, at longer immersion times, larger fractions of fibres are dissolved to form an amorphous matrix phase (non-crystalline domains). This directly results in a reduction of the overall crystallinity of the composites which was calculated from the XRD data and is shown in Figure 3.

Processing X-ray diffraction data by means of Scherrer's equation (Equation 1) also reveals that the lateral crystallite size normal to the (200) plane, in cellulose composites is reduced with immersion time (Figure 3). The size (width) of the cellulose crystallites was estimated from the width of the peak at $2\theta = 22.8°$ at half-height using the following equation.

$$D \text{ (crystal size)} = \lambda / \beta . \cos \theta \qquad \text{(Equation 1)}$$

where $\lambda = 1.5418$ Å, β: corrected integral width, θ: Bragg angle for the 200 reflection [25].

At longer immersion times, more cellulose is dissolved and hence smaller cellulose crystallites remain with larger non-crystalline domains being formed. This is also illustrated by the X-ray diffraction photographs of the composites (Figure 4) which indicate that the intensity of the non-crystalline scattering increased with immersion time. Furthermore, the reduction in the sharpness of the reflections for the composites prepared with longer immersion time also indicates lower molecular orientations in these composites. This is caused by an increase in the fraction of the formed amorphous phase (no orientation) with immersion time [32]. Correspondingly, the scanning electron micrographs (SEM) of the cross-section of the composites (Figure 5) show that longer immersion times lead to a reduction in fibre size and the formation of thicker matrix layers between the remaining fibre cores. From these scanning electron micrographs, the estimated volume fractions of the composites were determined by distinguishing each fraction and weighing. These results are illustrated in Figure 6.

As shown in Figure 7, in plant fibres, the outer layers of the fibres mainly consists of unordered or poorly oriented crystalline cellulose when compared to the inner core layers [8,30-31]. This should be beneficial for our surface selective

dissolution process as in this approach, only the thin, less oriented, outer layers of the fibres are dissolved which reform into a matrix phase, leaving the majority of the oriented high crystalline core of the fibre unaffected. From X-ray diffraction results, the composites prepared with 1 to 6 hours immersion time still exhibit a high crystalline character which is close to that of the original ramie fibres [25]. The scanning electron micrographs of these composites also reveal that the original fibres are largely retained. This would certainly explain that the fibre's strength is essentially maintained in the composites.

The tensile tests of the composites tested in the longitudinal (fibre) direction (Figure 8) show that the composite prepared with 2 hours immersion time exhibits the best properties. At this preparation condition, the amount of outer layer of the fibres which is dissolved to create a matrix phase is adequate to bond the remaining core fibres efficiently together (Figure 5; 2h), leading to a good interfacial bond and stress transfer in the composite. As also shown in Figure 6, the amount of voids in the composites are decreased from 6 vol.% to less than 1 vol.% for 2 hours immersion time and longer. Moreover, after partial dissolution of 2 hours, still only a relatively small amount of fibre is dissolved, leading to a high fibre volume fraction in the composite of ~84% (Figure 6). The good interfacial interaction together with the high fibre volume fraction and high remaining fibre strength, results in an optimum in properties for the composites with a high longitudinal tensile strength and Young's modulus. For the composite of 1 hour immersion time, a smaller amount of fibre surface is dissolved to form a matrix phase which apparently is not sufficient to provide a good interfacial bonding between the fibres in the composite. As illustrated by the SEM photographs (Figure 5), the composite of 1 hour immersion time displays cracks and voids in

between the fibres over the cross-sectional area. Only a discontinuous phase of very thin films of regenerated cellulose is formed between the fibres. Usually, a discontinuous phase connecting fibres together such as in particle board, is considered as a binder rather than a matrix phase. Although, for some of the all-cellulose composites here, the matrix is more like a binder, we will refer to it in this paper as a matrix. For the composite prepared with 1 hour immersion time, the SEM photograph (Figure 5; 1h) obviously points-out an inadequate formation of a matrix phase in this composite which causes a reduction in its stress transfer capability. The failure mode of this composite appears brush-like with extensive debonding along the fibres as shown in Figure 9. Due to the poor bonding between the fibres, this composite exhibits inferior mechanical properties compared to the composite of 2 hours immersion time even though for the 1 hour condition a smaller fraction of the fibres is dissolved. On the other hand, composites prepared at 3 hours immersion time results in enhanced interfacial bonding between fibre and matrix since a large fraction of the fibre surfaces is dissolved, forming a matrix phase to unite the aligned fibres. The SEM photographs in Figure 5 reveal that cracks and voids over the cross-sectional area of the composites were found to diminish and a thicker matrix phase between the reinforcing fibres is observed. In addition, Figure 9 illustrates that the failure mode of these composites tends to become more brittle with less debonding between fibre and matrix phases and a smaller amount of fibre pull-out, indicating strong interfacial adhesion [10,18,25] when the immersion time is increased. However, with increasing immersion time more of the fibre core is dissolved and as a result a significant reduction in composite strength is found compared to the original fibre strength. This causes an overall reduction in longitudinal composite properties, which ultimately gets close to that of the pure cellulose matrix. In

Figure 10, the stress-strain curves of the composites and the pure cellulose matrix show that the behaviour of the composites becomes similar to that of the pure cellulose matrix when the immersion time is increased. With increasing immersion time, the remaining fibre volume fraction in the resulting composites is reduced, which according to the 'rule of mixtures' theory for unidirectional composites, should lead to a linear reduction in mechanical properties of the composites [33].

A good indication for the level of interfacial adhesion between fibres in a composite can be determined through the evaluation of the transverse properties of a unidirectional composite laminate as shown in Figure 8. In this case, the composites prepared with the longer immersion times exhibit the better transverse tensile strength. The transverse tensile strength of composites prepared with 3 to 6 hours immersion time remain fairly constant and around 29-33 MPa, while longer immersion time results in the composites' properties approaching those of pure cellulose matrix properties. The transverse tensile strength of the composites of 9 and 12 hours immersion time were in 37 and 40 MPa, respectively, compared to pure cellulose matrix strength of 59 MPa. The improvement in the transverse tensile strength with immersion time implies a better interfacial adhesion in these composites. In addition, the observation of optical transparency (Figure 11) is another indication for an improved interfacial adhesion of the composites, as this transparency requires a perfect interphase with a perfect bonding between matrix and fibre [27,29]. Nevertheless, the elongation at break of the transverse composites is very low compared to that of the pure cellulose matrix, even for the composites prepared with the longest immersion times of 12 hours. This is due to the highly oriented character of the fibres which causes cracks to be easily initiated and

propagated along these anisotropic fibres compared to a crack propagating in an isotropic cellulose matrix.

According to the previous work of Nishino *et al.* [25], the all-cellulose composites prepared by impregnation resulted in a transverse tensile strength of nearly 12 MPa which was further improved to around 17 MPa after pre-treatment of the fibres. In this work, the composites of 2 and 3 hours immersion time already exhibit a better transverse tensile strength than the composites prepared by matrix impregnation with values of approximately 22 MPa and 31 MPa, respectively. It appears that the present preparation method can provide a much better interfacial adhesion between the fibres and the matrix than in the previously used impregnation method because the selective dissolution method results in an interphasial region, which minimises stress concentrations and voids that may lead to the initiation of cracks. The strong interfacial bond in these composites can be ascribed to the presence of strong hydrogen bonding within the cellulose fibre, matrix phase and interphasial region [12]. The tensile strength (in the longitudinal direction) of previously reported all-cellulose composites prepared by a cellulose matrix impregnation technique averaged 480 MPa [25] and 440 MPa [26]. For the present work a composite of 2 hours immersion time, results in a similarly high average longitudinal tensile strength of 460 MPa. This value is relatively high especially if we bear in mind that in this case the slightly oriented fibre skins were dissolved to form the matrix, while in another method the oriented fibres were kept intact and impregnated with an isotropic cellulose matrix. However, this reason appears to cause only a slight difference in tensile strength compared to the composites prepared with the impregnation technique which indicates that the surface selective dissolution process at the optimum condition only affects the low oriented fibre skins with the high

oriented core of the fibre remaining intact. Supposedly after 2 hours immersion time, the present preparation method results in the dissolution of only the thin outer layer of the fibres, which mainly consists of disordered or less oriented crystalline cellulose that does not contribute that much to the original fibre's strength. With only the less oriented fibre skin transformed into an isotropic matrix phase the highly crystalline core fibre remains largely unaffected and imparts a highly efficient reinforcing effect into the composites [8,30-31].

Figure 12 shows a comparison in mechanical properties of the all-cellulose composites prepared in this work to all-cellulose composites (ACC) in previous works and other unidirectional natural fibres based composites. For comparison, all composites are unidirectional except for two all-cellulose composites (in the rectangular box) which reinforcements are randomly oriented. The all-cellulose based composites (in the grey area) exhibit superior performances over other unidirectional natural fibres based composites especially, the three all-cellulose composites (in the circle) from Qin *et al.* [26], Gindl *et al.* [34] and the present study.

4. Conclusions

All-cellulose composites were successfully prepared by a surface selective or partial dissolution method of aligned fibres. During preparation, as the immersion time of the aligned ramie fibres in the solvent is increased, larger fractions of the fibre skin are dissolved to form a matrix phase resulting in an assembly of highly oriented fibre cores imparting an effective reinforcing effect to the all-cellulose composites. It was found that with increasing dissolution time a better interfacial adhesion between cellulose fibre and matrix was created which allows for a good stress transfer capability in the composite. Longitudinal tensile tests on unidirectional laminates showed that an

immersion time of 2 hours is the optimum processing condition to produce all-cellulose composites with the best overall properties using lithium chloride/*N,N*-dimethylacetamide as a solvent. At this condition, the amount of fibre surface selectively dissolved to form the matrix phase is adequate to provide sufficient interfacial adhesion to the composite, while the remaining fibre cores maintain most of their initial strength. The obtained all-cellulose composites show excellent mechanical properties which are similar or better than those prepared by a previously reported cellulose matrix impregnation method. The improvement in interface dominated properties like the transverse tensile strength indicates the stronger interfacial interaction in the composites obtained by the present surface selective dissolution preparation method. The outstanding properties of the all-cellulose composites originate from excellent mechanical properties of cellulose itself, the creation of a strong interface between the chemically identical cellulose reinforcement and matrix, resulting in a high efficiency of cellulose fibres in combination with very high fibre volume fractions.

References

[1]   Heijenrath R, Peijs T. Natural-fibre-mat-reinforced thermoplastic composites based on flax fibres and polypropylene. Adv Compos Lett 1996;5(3):81-85.

[2]   Peijs T, Garkhail S, Heijenrath R, van den Oever M, Bos H. Thermoplastic composites based on flax fibres and polypropylene: Influence of fibre length and fibre volume fraction on mechanical properties. Macromol Symp 1998;127:193-203.

[3]   Garkhail SK, Heijenrath RWH, Peijs T. Mechanical properties of natural-fibre-mat-reinforced thermoplastics based on flax fibres and polypropylene. Appl Compos Mater 2000;7(5-6):351-372.

[4]   Stamboulis A, Baillie CA, Garkhail SK, Van Melick HGH, Peijs T. Environmental durability of flax fibres and their composites based on polypropylene matrix. Appl Compos Mater 2000;7(5-6):273-294.

[5]   Peijs T. Composites turn green. e-Polymers 2002;T_002:1-12.

[6]   Singleton ACN, Baillie CA, Beaumont PWR, Peijs T. On the mechanical properties, deformation and fracture of a natural fibre/recycled polymer composite. Compos Part B-Eng 2003;34(6):519-526.

[7]   Mohanty AK, Khan MA, Hinrichsen G. Surface modification of jute and its influence on performance of biodegradable jute-fabric/Biopol composites. Comp Sci Technol 2000;60:1115-1124.

[8]   Lu X, Zhang MQ, Rong MZ, Shi G, Yang GC. Self-reinforced melt processable composites of sisal. Comp Sci Technol 2003;63:177-186.

[9]   Toriz G, Arvidsson R, Westin M, Gatenholm P. Novel cellulose ester-poly(furfuryl alcohol)-flax fiber biocomposites. J Appl Polym Sci 2003;88:337-345.

[10] Wibowo AC, Mohanty AK, Misra M, Drzal LT. Chopped industrial hemp fiber reinforced cellulosic plastic biocomposites: thermomechanical and morphological properties. Ind Eng Chem Res 2004;43:4883-4888.

[11] Nishino T, Hirao K, Kotera M, Nakamae K, Inagaki H. Kenaf reinforced biodegradable composite. Comp Sci Technol 2003;63:1281-1286.

[12] Soykeabkaew N, Supaphol P, Rujiravanit R. Preparation and characterization of jute- and flax-reinforced starch-based composite foams. Carbohyd Polym 2004;58:53-63.

[13] Puglia D, Tomassucci A, Kenny JM. Processing, properties and stability of biodegradable composites based on Mater-Bi and cellulose fibres. Polym Advan Technol 2003;14:749-756.

[14] Lu Y, Weng L, Cao X. Morphological, thermal and mechanical properties of ramie crystallites-reinforced plasticized starch biocomposites. Carbohyd Polym 2006;63:198-204.

[15] Averous L, Boquillon N. Biocomposites based on plasticized starch: thermal and mechanical behaviours. Carbohyd Polym 2004;56:111-122.

[16] Luo S, Netravali AN. Interfacial and mechanical properties of environment-friendly green composites made from pineapple fibers and poly(hydroxybutyrate-co-valerate) resin. J Mater Sci 1999;34:3709-3719.

[17] Wollerdorfer M, Bader H. Influence of natural fibres on the mechanical properties of biodegradable polymers. Ind Crop Prod 1998;8:105-112.

[18] Mohanty AK, Wibowo A, Misra M, Drzal LT. Effect of process engineering on the performance of natural fibre reinforced cellulose acetate biocomposites. Compos Part A-Appl S 2004;35:363-370.

[19] Eichhorn SJ, Young RJ. Composite micromechanics of hemp fibres and epoxy resin microdroplets. Comp Sci Technol 2004;64:767-772.

[20] Shanks RA, Hodzic A, Ridderhof D. Composites of poly(lactic acid) with flax fibres modified by interstitial polymerization. J Appl Polym Sci 2006;99:2305-2313.

[21] Ward IM, Hine PJ. Novel composites by hot compaction of fibers. Polym Eng Sci 1997;37(11):1809-1814.

[22] Ward IM, Hine PJ. The science and technology of hot compaction. Polymer 2004;45:1413-1427.

[23] Peijs T. Composites for recyclability. Materials Today 2003;April:30-35.

[24] Cabrera N, Alcock B, Loos J, Peijs T. Processing of all-polypropylene composites for ultimate recyclability. Proc Inst Mech Eng Part L: J Materials: Design and Applications 2004;218:145-155.

[25] Nishino T, Matsuda I, Hirao K. All-cellulose composite. Macromolecules 2004;37:7683-7687.

[26] Qin C, Soykeabkaew N, Xiuyuan N, Peijs T. The effect of fibre volume fraction and mercerization on the properties of all-cellulose composites. Carbohyd Polym 2008;71:458-467.

[27] Gindl W, Keckes J. All-cellulose nanocomposite. Polymer 2005;46:10221-10225.

[28] Matsumura H, Sugiyama J, Glasser WG. Cellulosic nanocomposites. I. Thermally deformable cellulose hexanoates from heterogeneous reaction. J Appl Polym Sci 2000;78:2242-2253.

[29] Nishino T, Arimoto N. All-cellulose composite prepared by selective dissolving of fiber surface. Biomacromolecules 2007;8:2712-2716.

[30] Klemm D, Schmauder H, Heinze T. Cellulose. Biopolymers, 1st edition, vol. 6. Wiley-VCH, Weinheim; 2003. p. 275-285.

[31] Krässig HA. Cellulose: Structure Accessibility and Reactivity. Gordon and Breach Science Publishers, Polymer Monographs, vol. 11; 1993. p. 167-323.

[32] Kong K, Davies RJ, McDonald MA, Young RJ, Wilding MA, Ibbett RN, Eichhorn SJ. Influence of domain orientation on the mechanical properties of regenerated cellulose fibers. Biomacromolecules 2007;8:624-630.

[33] Hull D, Clyne TW. Elastic deformation of long-fibre composites. An Introduction to Composite Materials, 2nd Edition; 1996. p. 60-77.

[34] Gindl W, Keckes, J. Drawing of self-reinforced cellulose films. J Appl Polym Sci 2007;103:2703-2708.

[35] Madsen B, Lilholt H. Physical and mechanical properties of unidirectional plant fibre composites-an evaluation of the influence of porosity. Comp Sci Technol 2003;63:1265-1272.

[36] Oksman K, Wallstrom L, Berglund LA, Filho RDT. Morphology and mechanical properties of unidirectional sisal–epoxy composites. J Appl Polym Sci 2002;84:2358-2365.

[37] Brahim SM., Cheikh RB. Influence of fibre orientation and volume fraction on the tensile properties of unidirectional Alfa-polyester composite. Comp Sci Technol 2007;67:140-147.

[38] Van de Weyenberg I, Truong TC, Vangrimde B, Verpoest I. Improving the properties of UD flax fibre reinforced composites by applying an alkaline fibre treatment. Compos Part A-Appl S 2006;37:1368-1376.

Caption of Figures

Fig. 1   Surface selective dissolution process to prepare all-cellulose composites.

Fig. 2   X-ray diffraction profiles of the all-cellulose composites, indicating the reduction in crystallinity of the composites with immersion time.

Fig. 3   Effect of immersion time on % crystallinity and cellulose crystallite size (nm) of the all-cellulose composites.

Fig. 4   X-ray diffraction photographs of the all-cellulose composites, showing the increase in intensity of the non-crystalline scattering with immersion time.

Fig. 5   Scanning electron micrographs of the cross-section of the all-cellulose composites, showing the longer the immersion time, the more of the matrix phase is formed and the better the interfacial bonding of the composites.

Fig. 6   Structural information of the all-cellulose composites prepared with various immersion times. The values in the figure are estimated from scanning electron micrographs of the composites for an equivalent cross-sectional area of 6,250 μm^2 by distinguishing each fraction and weighing.

Fig. 7   Structural design of plant cell wall exemplified by cotton fibres. C = cuticula layer (rich in pectins and waxes); P = primary cell wall layer; S1 = secondary cell wall layer 1; S2 = secondary cell wall layer 2 (main body; consist of

microfibril helically oriented at an angle close to the fibre axis); R = reversal of the fibril spiral; L = lumen [24-25].

Fig. 8 Effect of immersion time to the tensile properties of the all-cellulose composites in longitudinal and transverse tests, showing the optimum preparation condition of 2 hours immersion time resulting in the best overall properties of the composites.

Fig. 9 Photographs of failed specimens of the all-cellulose composites, showing the more brittle failure mode with less debonding and a smaller amount of fibre pull-out, indicating stronger interfacial adhesion, with increasing immersion time.

Fig. 10 Stress-strain curves of the all-cellulose composites and the pure cellulose matrix.

Fig. 11 Optical transparency observation of the all-cellulose composites, indicating the formation of a perfect interfacial region.

Fig. 12 Comparison in mechanical properties of the all-cellulose composites prepared in this work to all-cellulose composites in the previous works and other unidirectional (UD) natural fibres based composites. It illustrates the superior performances of the all-cellulose based composites (in the grey area).

Table 1 The properties and characteristic of the as-receive ramie fibres
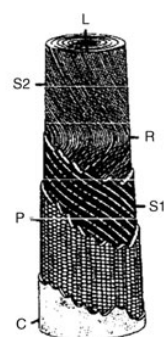(reported with the standard deviation in parentheses)

Tensile strength (MPa)	768 (154)
Young's modulus (GPa)	42.0 (7.9)
Elongation at max. load (%)	2.57 (0.66)
Average diameter (μm)	24.4 (2.8)

Figure 1

Cellulose
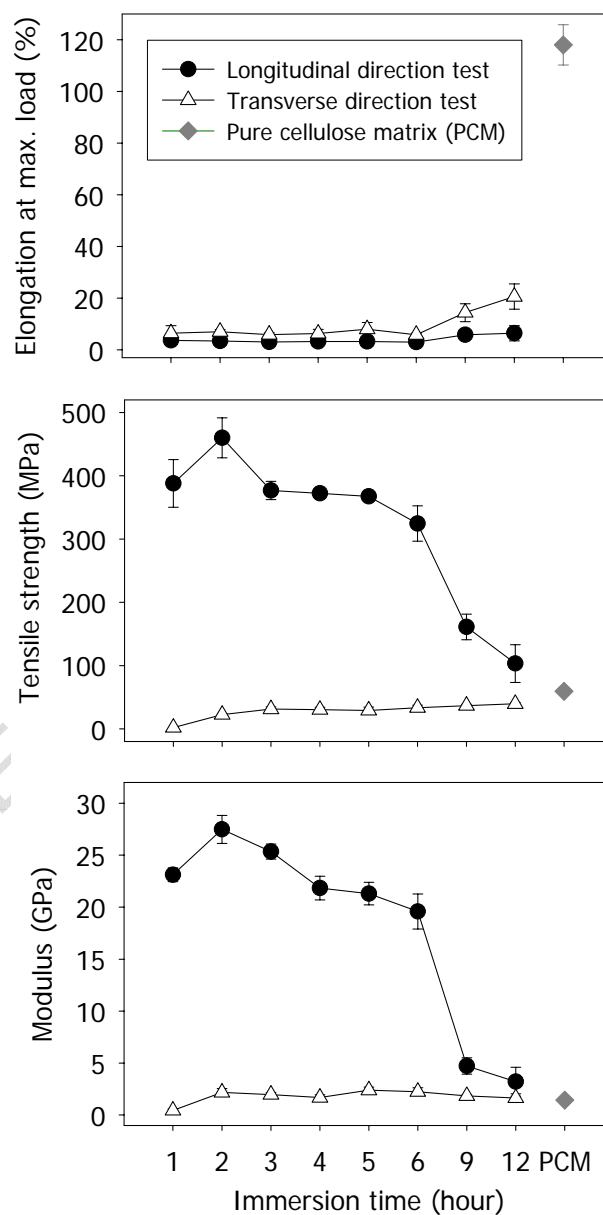Fibres

Surface Selective
Dissolution

All-Cellulose
composites
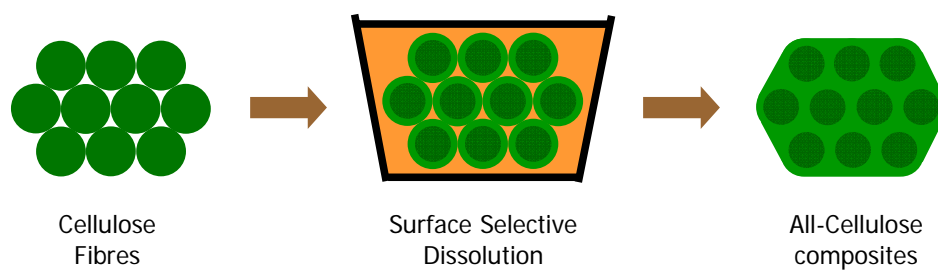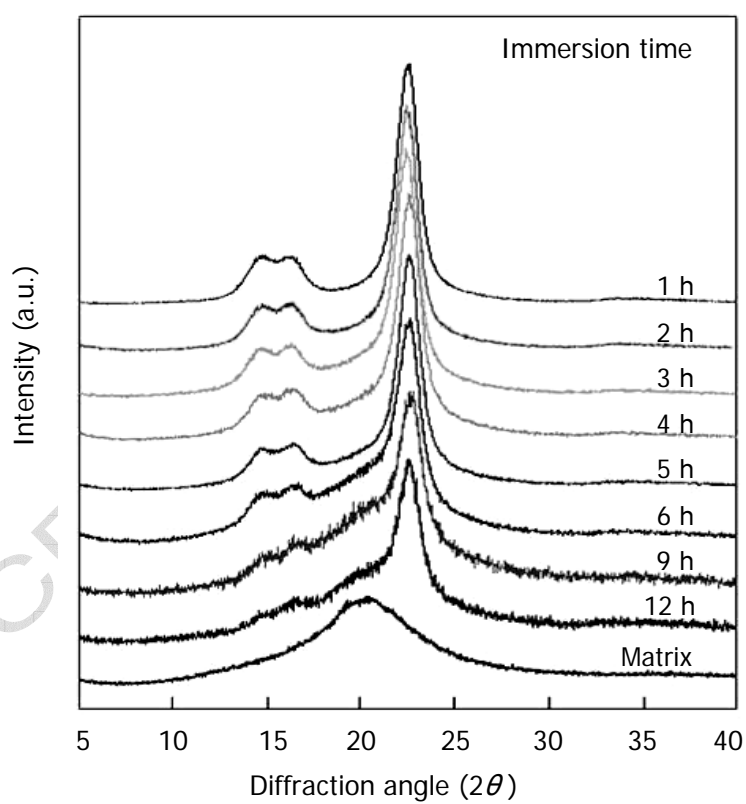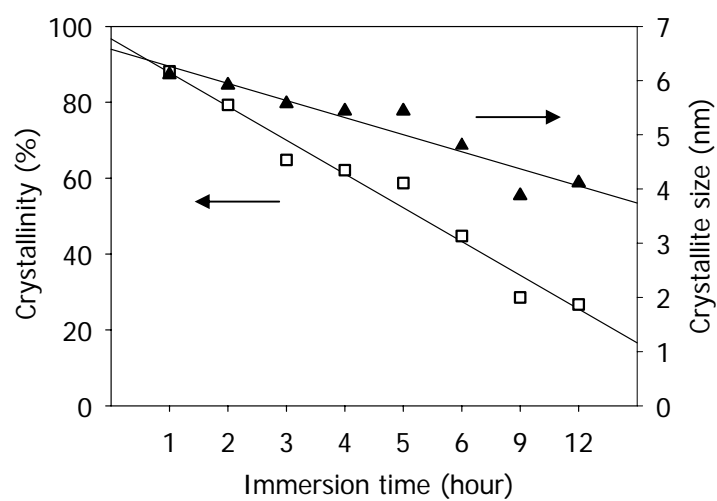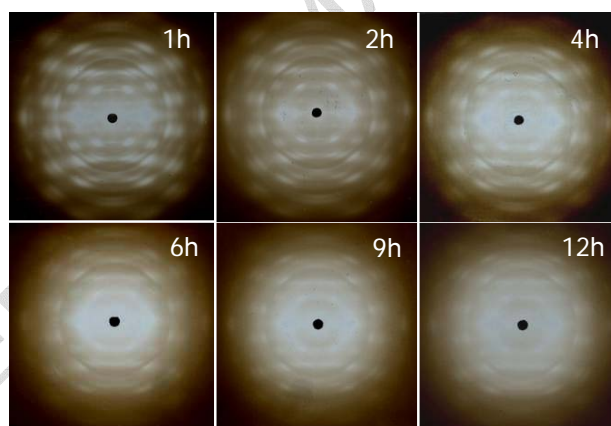
Figure 2

Figure 3
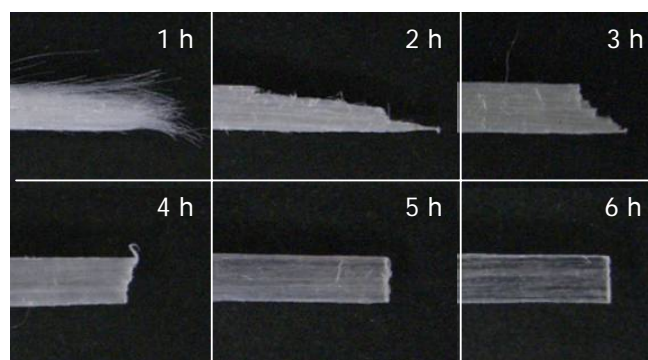

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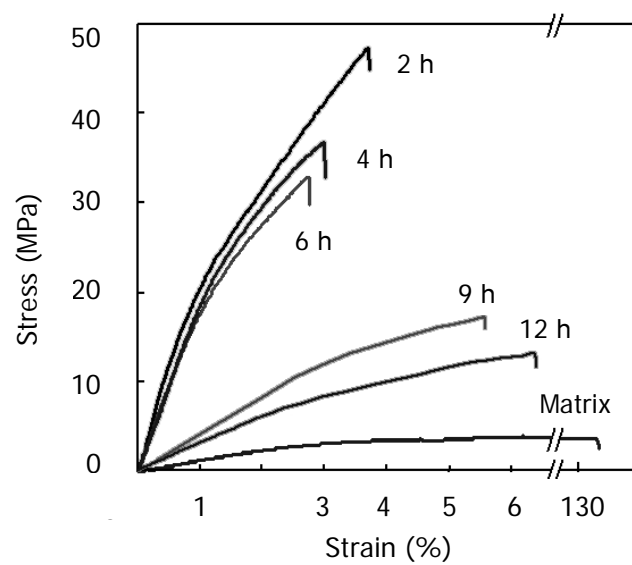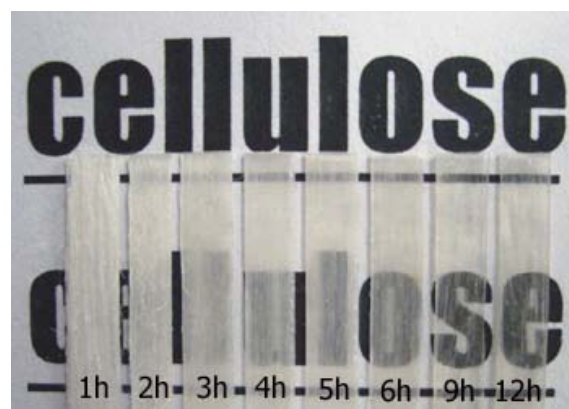
Figure 5

Figure 6

24
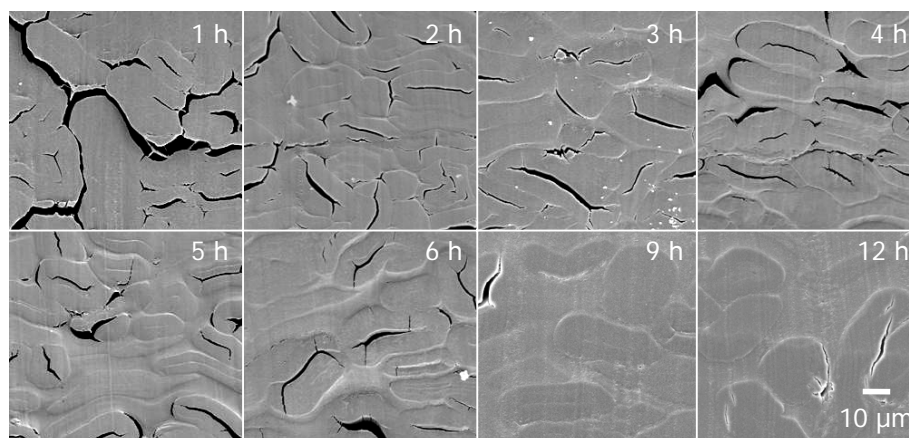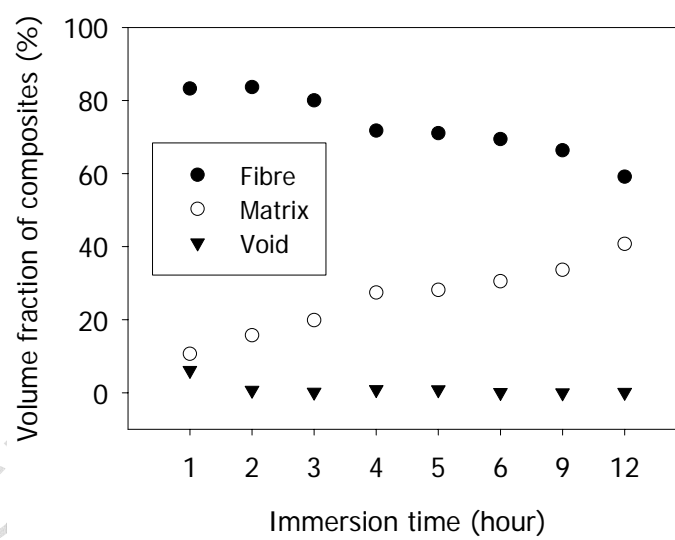
Figure 7

Figure 8

Figure 9

Figure 10

Figure 11

Figure 12