

PHASE CHARACTERISATION OF ALL-CELLULOSE COMPOSITES

Benoît J.-C. Z. Duchemin*, Roger Newman, Mark P. Staiger***

*Department of Mechanical Engineering, University of Canterbury, Private Bag 4800, Christchurch, New Zealand.

**Scion, Private Bag 3020, Rotorua, New Zealand.

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Abstract

All-cellulose composites were prepared by partial dissolution of microcrystalline cellulose (MCC) in an 8.0 wt. % LiCl/DMAc solution. Cellulose concentrations (c) of 5, 10, 15 and 20 wt. % were selected and different dissolution times were trialled. WAXD and ^{13}C solid-state NMR were used to characterize molecular packing. Consolidation of MCC powder in a composite occurs by progressive transformation of the cellulose I crystals into a matrix of paracrystalline and amorphous cellulose. Both WAXD and ^{13}C solid-state NMR point out sufficient differences between the amorphous and the paracrystalline states. The extent of the transformation was observed to increase with longer dissolution times or lower cellulose concentrations. More profound changes are visible when $c < 15$ wt. %. For a given dissolution time, the specific mechanical properties generally increased with the crystallinity of the material.

1. Introduction

All-cellulose composites are a new class of biodegradable materials taking advantage of the exceptional strength and stiffness of the cellulose polymer. [1] Those composites mimic cellulosic fibres found in the nature. Indeed, both are an assembly of highly crystalline cellulose embedded into polysaccharides of lower crystallinity. The first one confers stiffness and strength to the material whereas the latter one contributes to the overall viscoelasticity of the material.

Previous works have shown that all-cellulose composites could be prepared by embedding long natural fibres (e.g. ramie) in a matrix of completely dissolved cellulose (e.g. coniferous pulp) prior to

consolidation.[2] Another possibility consists in the partial dissolution of highly crystalline cellulose, the product of which will form the low crystallinity cellulose that will act as the matrix.[3-5] In the present work, changes in cellulose molecular conformation after partial dissolution of microcrystalline cellulose (MCC, Avicel) in the solvent lithium chloride/*N,N*-dimethylacetamide (LiCl/DMAc) were investigated. The properties of several MCC composites were characterised by wide-angle x-ray diffraction (WAXD), solid-state cross-polarized magic angle spinning (CP-MAS) ^{13}C NMR spectra (NMR), transmission electron microscopy (TEM) and mechanical testing.

2. Experimental Procedures

2.1. Material Preparation

Cellulose dissolution using DMAc initially involves an activation step in which the cellulose structure is first swollen via solvent exchange. [6, 7] The increased molecular mobility of cellulose allows the LiCl/DMAc solvent to penetrate the cellulose structure more easily.[8, 9] In the present work, microcrystalline cellulose (MCC) powder (Avicel, Merck, particle size between 20 and 160 μm) was immersed in distilled water at 20°C for 48 hrs and vacuum-filtered through Whatman No. 1 filter paper, twice immersed in acetone (Biolab, laboratory grade) at 20°C for 24 hrs and filtered through Whatman No. 1 filter paper to remove the acetone each time, twice immersed in DMAc (Merck, synthesis grade) at 20°C for 24 hrs and each time filtered through Whatman No. 1 filter paper afterward, vacuum-dried for 48 hrs at 60°C and then sieved (90 μm). The activated MCC was vacuum-dried for a further 48 hrs at 60°C and finally sealed

in a container for storage. The DP was determined using Bianchi et al. (1985) method and found to be 163. [10] Partial dissolution occurred by immersing the cellulose in an 8 wt. % LiCl/DMAc solution.

2.1.1. Method 1

A preparation aimed at looking at a range of crystalline conformations was first prepared. Cellulose concentration (abbreviated as c in the rest of the text) amounted to 5, 10, 15 and 20 wt. % of the total mixture. Dissolution times of 1, 4, 8 and 48 hrs were selected. Dissolution occurred under reduced pressure. After the completion of this step, the partially dissolved cellulose was precipitated in water and thoroughly rinsed for 48 hrs. The final composites were obtained by vacuum drying 48 hrs at 60 °C.

2.1.2. Method 2

A portion of activated MCC was immersed under constant stirring in a small beaker containing sufficient LiCl/DMAc to achieve cellulose concentrations of $c = 10\%$, LiCl and DMAc. The solution was stirred for 3 min, poured in Petri dishes and placed under dry nitrogen for 1 and 8 hrs at 20 °C. The precipitation of the dissolved cellulose began initially by placing the Petri dishes under controlled atmosphere (20 °C and 76 % R.H.) for 24 hrs. This step completely precipitated the cellulose material. It was then placed under running water for 48 hrs for thorough rinsing and then freeze-dried in order to obtain a relatively thick (3-4 mm) porous structure.

2.1.3. Method 3

A second preparation is presented here that was aimed at illustrating the extent of the dissolution on the mechanical properties. Solutions of cellulose with $c = 5, 10, 15$ and 20 wt. % were stirred for 3 min, poured in Petri dishes and placed under controlled atmosphere (20 °C and 33 % R.H.) for 24 hrs. A low humidity was initially selected in order to initiate gentle precipitation with better gel form retention. After the initial 24 hrs step, the gels were placed overnight at 20 °C and 76 % R.H.. At this stage, the cellulose appeared to be completely precipitated. After the completion of this step, the precipitated cellulose was thoroughly rinsed for 48 hrs under water. The final composites were obtained in the form of a porous structure by freeze-drying.

2.2 Materials Characterisation

X-ray patterns were obtained with a Philips PW1729 using a Cu target ($\lambda=1.54040$ Å), voltage of 50 kV and current of 40mA over the range $5^\circ < 2\theta < 50^\circ$ in 0.02° steps. CrI as defined by Segal

(1959) was used as a measure of the crystallinity. [11] The measure was performed manually on graphs plotted from Excel. Crystal thickness D across the (200) plane is obtained by using the Scherrer equation. WAXD was performed on all the materials referred to in this study.

Solid state CP-MAS ^{13}C NMR spectra were obtained on a Bruker Avance DRX200 FT-NMR spectrometer at a frequency of 50.3 MHz and at a magic-angle spinning frequency of 5 kHz. Transients from a minimum of 10,000 pulses were averaged in both cases. Differentiation between the crystalline and non-crystalline materials in the spectra was enhanced by proton spin relaxation editing (PSRE). This method produces two subspectra, **S** and **S'**. The crystal signal is partly suppressed from **S'** by relatively fast proton spin relaxation in the crystalline region. A deconvolution technique is used to discriminate further between non-crystalline and crystalline materials and produce a subspectra **A** (resp. **B**) where the poorly-ordered (resp. well-ordered) content is excluded. PSRE is a powerful technique that provides both the crystalline cellulose fraction F_c , X_c , the percentage of interior cellulose chains as a percentage of the total crystalline cellulose and L_c , an estimate of the apparent crystal size. Details about this procedure can be found in the relevant literature. [12-14] NMR was only performed on the initial composites.

TEM images were obtained on a FEI Morgagni with a 100 kV acceleration voltage. The specimens were prepared by embedding the composites in spur resin, microtoming and staining in uranyl acetate.

Mechanical testing was performed in accordance with the ASTM-790 standard on the foam material in three-point bending with a table-top Instron equipped with 500 N load cells. A span length of 35 mm and a cross-head speed of 10 mm/min were selected. A minimum of 5 specimens was tested for each type of composite after conditioning. The values of the flexural strength σ_f and Young's modulus in bending E_b were expressed as a function of the material density, which will be referred in the text as specific flexural strength $\dot{\sigma}_f$ and specific Young's modulus \dot{E}_b . ϵ_f is the flexural strain at break.

(a)

3. Results and Discussion

3.1. Crystallography

MCC is a pure form of cellulose I, which is the native cellulose allomorph, and so is the pre-treated

MCC. Both NMR and WAXD point out that the matrix is a mixture of amorphous and paracrystalline cellulose.

Table 1. Data for starting materials and all-cellulose composites prepared by partial dissolution for 8 h at cellulose concentrations c expressed as % of the total weight of cellulose, LiCl and DMAc.

Sample	CrI (%)	D (nm)	F	X (%)	L (nm)
MCC	87	4.5	(0.84) a	(65) ^a	(5.9) ^a
Activated	80	4.8	0.73	67	6.3
$c = 20\%$	68	- ^b	0.56	61	5.2
$c = 15\%$	54	- ^b	0.52	49	3.8
$c = 10\%$	32	- ^b	0.24	32	2.6
$c = 5\%$	35	- ^b	0.37	24	2.3

^a literature values (Newman and Hemmingson 1995)

^b not done because of peak overlap

The matrix material formed during dissolution distinguishes itself from an amorphous material both in the NMR and in the WAXD studies. In the NMR study (Fig. 1a), peak placement showed no evidence of other allomorphs such as cellulose II or III₁ in the composites.

The lower C-4 peak is found in the paracrystalline region centred around 84 ppm, which corresponds to cellulose I crystallite exterior chains with hydroxymethyl groups in the *gauche-gauche* conformation. [15] The C-6 signal area was found in a peak at 62 ppm, which is also consistent with chains exposed on surfaces of cellulose I.[15]

As $T_2(H) = 8.5 \mu s$ (resp. $19 \mu s$) for crystalline cellulose (resp. amorphous matrix polysaccharides), a value of $T_2(H) = 11 \mu s$ for the matrix suggests a paracrystalline rather than an amorphous state. Those results indicate the presence of very thin crystallites of cellulose I where all the cellulose chains are exposed to the surface rather than amorphous cellulose.

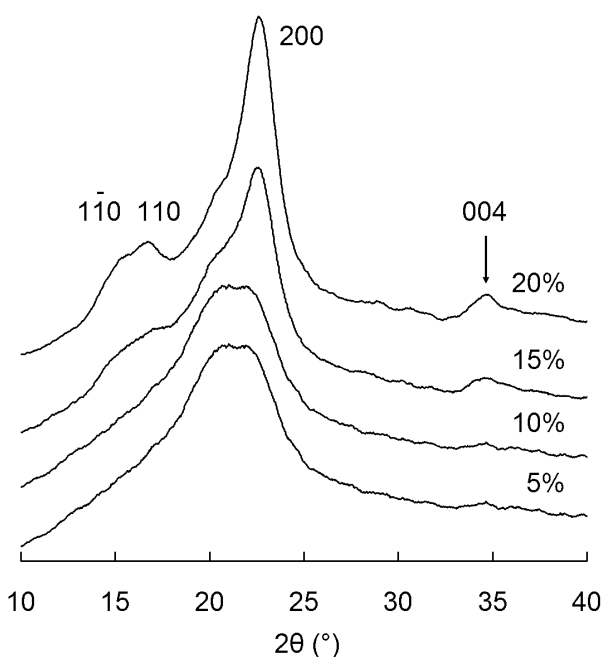
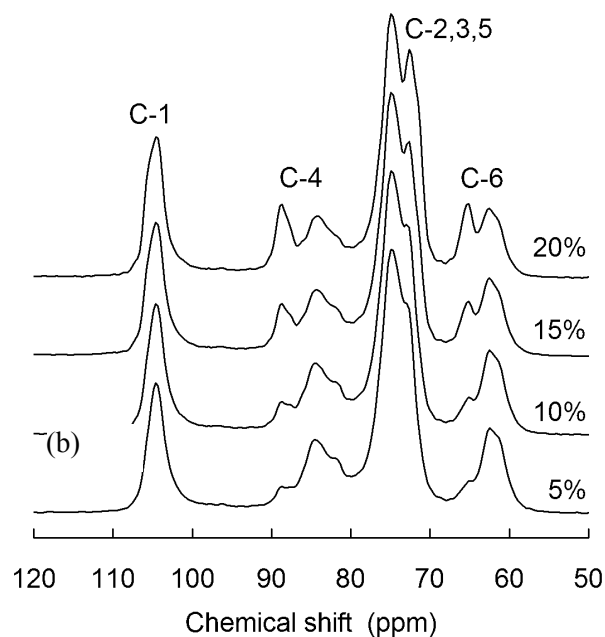


Fig. 1 a) WAXS diffractograms of all-cellulose composites prepared as described under method 1 with values of c shown above each trace. b) Solid-state ^{13}C NMR spectra of the same all-cellulose composites prepared from activated cellulose mixed with solvent at the weight % values shown above each trace and left for 8 h of dissolution.

In the WAXD study (Fig. 1b), the main (200) peak at $2\theta = 20.8^\circ$ was 5.0° wide at half maximum height, and this width was too small for the peak to be assigned to amorphous cellulose.

Ball-milled cellulose is commonly used as a reference standard for amorphous cellulose. The peak position has been reported as $2\theta = 18^\circ$ [11, 16] or $2\theta = 20^\circ$ [17], but it is generally agreed that the width is approximately 10° . We must conclude that the cellulose matrix in the composites is not amorphous but paracrystalline. A peak at (004) indicative of long-range order disappears with decreasing concentration, which is also a hint for the presence of the paracrystalline state.

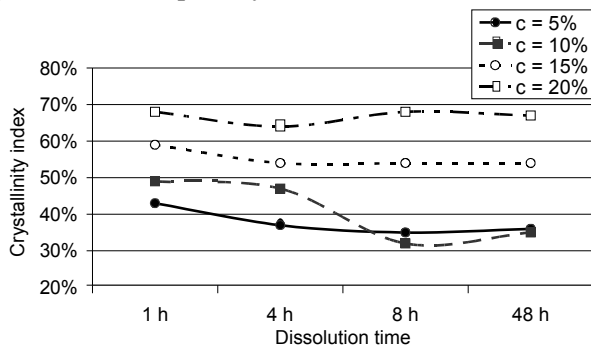


Fig. 2 CrI variation in the all-cellulose composites described in method 1.

PSRE-NMR and WAXD showed that crystallinity index decreases as the cellulose concentration is decreased or, in general, as the dissolution time is increased (Table 1 and Figure 2). This change is correlated with the creation of thinner crystals and holds true for the freeze dried materials (Fig. 3 and 4). The final composite is a mixture of cellulose I and cellulose IV₁, or poorly crystalline cellulose I. Crystallinity seems to stabilize at about 35-40 % when the cellulose weight concentration is inferior to 10 wt. %. There is a high correlation between those values of CrI and the product $F \cdot X$ ($r^2=0.95$). The latter one can be interpreted as the percentage of interior crystalline cellulose in the total crystalline fraction of the material. TEM (Fig. 5) seems to support the hypothesis of a poorly ordered matrix with highly crystalline and still undissolved remnants of MCC acting as the reinforcement.

3.2. Mechanical testing

The density of the foam materials was comprised between 150 kg/m^3 and 350 kg/m^3 . The freeze-dried composites exhibit superior mechanical properties despite a relatively high standard deviation due to the variability of the porous structure. The dominant mode of failure was the tension one. Method 2 yielded two materials with very similar CrI but slightly larger peak width

(abbreviated as HWH) for the composite obtained after the longest impregnation (Table 2). Larger strain, stiffness and elongation at break were explained by superior impregnation of the reinforcement for the longest dissolution time. The slight decrease in the CrI (or increase in HWH, see Fig. 3) might account for more of the paracrystalline matrix providing more viscoelasticity to the material. Longer dissolution times seem to improve the wetting of the fibres.

The materials obtained by method 3 generally had their specific strength and stiffness increasing with c . This increase is also correlated with a raise of the crystallinity index, as measured by x-ray (Fig. 4). This trend was expectable, as highly crystalline cellulose is known to be stiffer than its more paracrystalline counterparts.

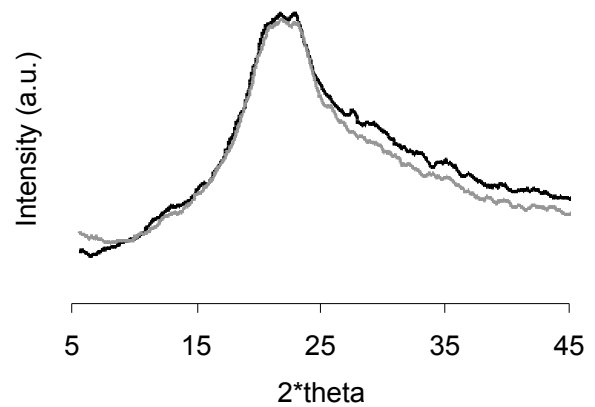


Fig. 3 WAXD patterns of the composites obtained from method 2 after 1 h under dry nitrogen (grey) and 8 h (black)

Table 2 Mechanical properties and crystallinity index essentially show the same trend when the dissolution time was increased.

	σ_f (MPa.m ³ /s)	E_b (MPa.m ³ /s)	ϵ_f	CrI
10 % 1 hr	0.017	0.901	2.88%	39%
10 % 8 hrs	0.037	2.096	3.22%	36%

The Young's modulus of amorphous cellulose was calculated to be $10.42 \pm 1.08 \text{ GPa}$ by Chen et al. [18] Using x-ray diffraction, Nishino measured the elastic modulus in the direction parallel to the chain axis of several cellulose polymorphs; cellulose I was found to have a modulus of 138 GPa whereas cellulose IV₁ exhibited a lower value at 75 GPa.[1] Ishikawa et al. (1997) published similar values and

ranking for polymorphs produced out of ramie fibre.[19]

Very low density ($\sim 300 \text{ kg/m}^3$) and somewhat comparable mechanical properties make this material comparable to dry coconut timber, balsa wood in longitudinal properties, wood in transverse direction and cancellous bone. [20]

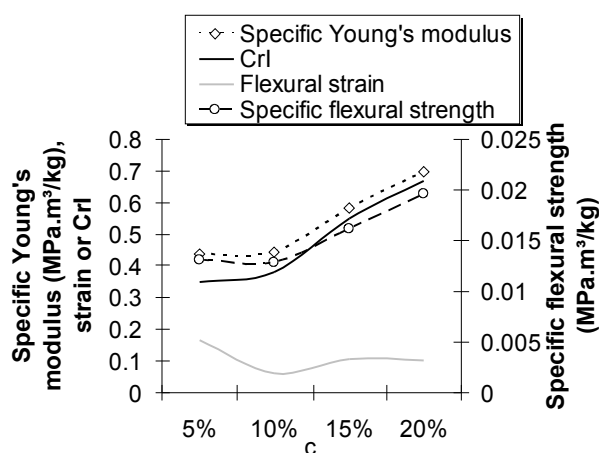


Fig. 4 Specific Young's modulus, specific flexural strength, flexural strain at break and CrI for the composites prepared as described in method 3.

4. Conclusions

As a conclusion, cellulose I sheets peel away from large highly oriented cellulose I crystallites during dissolution. Those sheets aggregate into low crystallinity cellulose I or IV₁ once precipitated and dried. This paracrystalline form of cellulose along with the amorphous one form the matrix of the composite. The extent of the transformation influences the mechanical properties of the composite materials. For a given impregnation time, both specific modulus and specific flexural strength increase with the cellulose concentration in the initial LiCl/DMAc mixture. This increase seems correlated to an increase of the CrI, inherent to composite materials with bigger cellulose I crystals. Higher dissolution times seem to provide better mechanical properties, supposedly because of better fibre wetting. By varying the cellulose concentration in the LiCl/DMAc mixture and the dissolution time, we have obtained a range of all-cellulose composites. Spectroscopy and mechanical testing unravelled some of the intimate molecular mechanisms leading to the consolidation of MCC powder into an all-cellulose composite. The studies

of partial cellulose dissolution are relatively new and constitute a field of constant research.

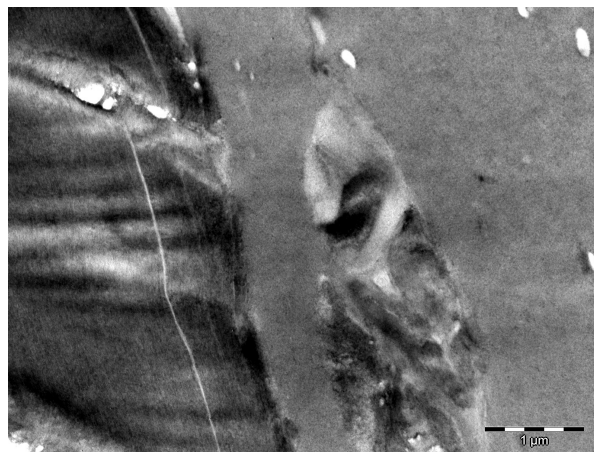


Fig. 5. TEM micrograph of an all-cellulose composite obtained by precipitating 5 wt. % MCC in an 8 wt. % LiCl/DMAc solution after 8 hrs of dissolution time. One of the rare remnants of the initial MCC highly oriented phase is embedded in a non-oriented matrix.

References

1. Nishino T., Takano K. and Nakamae K. "Elastic Modulus of the Crystalline Regions of Cellulose Polymorphs". *Journal of Polymer Science: Part B: Polymer Physics*. Vol. 33, pp. 1647-1651, 1995.
2. Nishino T., Matsuda I. and Hirao K. "All-cellulose composite". *Macromolecules*. Vol. 37, No. 20, pp. 7683-7687, 2004.
3. Nishino T. and Arimoto N. "All-cellulose composite by partial dissolving of fibers". *Proceedings of EcoComp2005*. Stockholm, 2004.
4. Gindl W. and Keckes J. "All-cellulose nanocomposite". *Polymer*. Vol. 46, No. 23, pp. 10221-10225, 2005.
5. Gindl W., Schoberl T. and Keckes J. "Structure and properties of a pulp fibre-reinforced composite with regenerated cellulose matrix". *Applied Physics a-Materials Science & Processing*. Vol. 83, No. 1, pp. 19-22, 2006.
6. Striegel A.M., "Advances in the understanding of the dissolution mechanism of cellulose in DMAc/LiCl." *J. Chil. Chem. Soc.* Vol. 48, No. 1, pp. 73-77, 2002.

7. Dupont A.-L. "Cellulose in lithium chloride/N,N-dimethylacetamide, optimisation of a dissolution method using paper substrates and stability of the solutions". *Polymer*. Vol. 44, No 15, pp. 4117-4126, 2003.
8. McCormick C.L., Callais P.A. and Hutchinson B.H. "Solution Studies of Cellulose in Lithium-Chloride and N,N-Dimethylacetamide". *Macromolecules*. Vol. 18, No. 12, pp. 2394-2401, 1985.
9. Ishii D., Tatsumi D. and Matsumoto T. "Effect of Solvent Exchange on the Solid Structure and Dissolution Behavior of Cellulose". *Biomacromolecules*. Vol. 4, No. 5, pp. 1238-1243, 2003.
10. Bianchi E. et al. "Mesophase Formation and Chain Rigidity in Cellulose and Derivatives .4. Cellulose in N,N-Dimethylacetamide Lithium-Chloride". *Macromolecules*. Vol. 18, No. 4, pp. 646-650, 1985.
11. Segal L., Creely J.J., Martin A.E. Jr. and Conrad M.C. "An empirical method for estimating the degree of crystallinity of native cellulose using the X-ray diffractometer". *Textile Res. J.* Vol. 29, pp. 786-794, 1959.
12. Newman R.H., Davies L.M. and Harris P.J. "Solid-State ¹³C Nuclear Magnetic Resonance Characterization of Cellulose in the Cell Walls of Arabidopsis thaliana Leaves". *Plant Physiol*. Vol. 111, No. 2, pp. 475-485, 1996.
13. Newman R.H. "Estimation of the lateral dimensions of cellulose crystallites using ¹³C NMR signal strengths". *Solid State Nuclear Magnetic Resonance*. Vol. 15, No. 1, pp. 21-29, 1999.
14. Newman R.H. and Hemmingson J.A. "Carbon-13 NMR distinction between categories of molecular order and disorder in cellulose". *Cellulose*. Vol. 2, pp. 95-110, 1995.
15. Newman R.H. and Davidson T.C. "Molecular conformations at the cellulose-water interface". *Cellulose*. Vol. 11, No. 1, pp. 23, 2004.
16. Mann J. "Modern methods of determining crystallinity in cellulose". *Pure and Applied Chemistry*. Vol. 5, pp. 91-105, 1962.
17. Schroeder L.R., Gentile V. and Atalla R.H. "Nondegradative preparation of amorphous cellulose". *Journal of wood chemistry and technology*. Vol. 6, pp. 1-14, 1986.
18. Chen W., Lickfield G.C. and Yang C.Q. "Molecular modeling of cellulose in amorphous state. Part I: model building and plastic deformation study". *Polymer*. Vol. 45, No. 3., pp. 1063-1071, 2004.
19. Ishikawa A., Okano T. and Sugiyama J., "Fine structure and tensile properties of ramie fibres in the crystalline form of cellulose I, II, III₁ and IV₁". *Polymer*. Vol. 38, No. 2, pp. 463-468, 1997.
20. Wegst, U.G.K. and Ashby M.F. "The mechanical efficiency of natural materials". *Philosophical Magazine*. Vol. 84, No. 21, pp. 2167 - 2186, 2004.