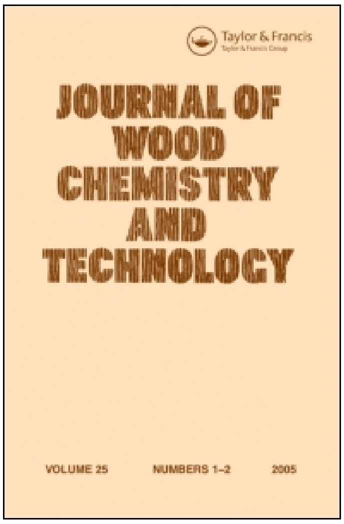
This article was downloaded by:
On: *25 January 2011*
Access details: *Access Details: Free Access*
Publisher *Taylor & Francis*
Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



Journal of Wood Chemistry and Technology
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597282

Preparation of Thermoplastic Magnetic Wood via Etherification and *In-Situ* Synthesis of Iron Oxide

Yusuke Matsumoto[a]; Yoshikuni Teramoto[a]; Yoshiyuki Nishio[a]
[a] Division of Forest and Biomaterials Science, Graduate School of Agriculture, Kyoto University, Kyoto, Japan

Online publication date: 20 November 2010

To cite this Article Matsumoto, Yusuke , Teramoto, Yoshikuni and Nishio, Yoshiyuki(2010) 'Preparation of Thermoplastic Magnetic Wood via Etherification and *In-Situ* Synthesis of Iron Oxide', Journal of Wood Chemistry and Technology, 30: 4, 373 — 381

To link to this Article: DOI: 10.1080/02773813.2010.523165

URL: http://dx.doi.org/10.1080/02773813.2010.523165

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: http://www.informaworld.com/terms-and-conditions-of-access.pdf

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

Journal of Wood Chemistry and Technology, 30: 373–381, 2010
Copyright © Taylor & Francis Group, LLC
ISSN 0277-3813 print / 1532-2319 online
DOI: 10.1080/02773813.2010.523165

Preparation of Thermoplastic Magnetic Wood via Etherification and *In-Situ* Synthesis of Iron Oxide

Yusuke Matsumoto, Yoshikuni Teramoto, and Yoshiyuki Nishio
Division of Forest and Biomaterials Science, Graduate School of Agriculture,
Kyoto University, Kyoto, Japan

Abstract: Wood flour (WF) was converted not only to thermoplastic material but also to carrier matrix for *in-situ* synthesis of iron oxide nano-particles by a set of etherification; namely, considerable hydroxypropylation and modest carboxymethylation. A sequence of procedure for the *in-situ* synthesis of iron oxides includes ferrous ion-absorption of the etherified WF, precipitation of ferrous hydroxide by an alkaline treatment, and oxidation of the ferrous hydroxide. Magnetometry measurements revealed that the magnetic woody composite showed superparamagnetism (SPM) at room temperature. The observation of SPM may be of significance in the perceptibility to an external magnetic stimulus only on demand and without energy loss.

Keywords: Etherification, iron oxide, magnetic nanocomposite, thermoplastic, wood flour

Downloaded At: 11:56 25 January 2011

INTRODUCTION

Cellulose has recently been reevaluated not only as a sustainable resource but also as a key component for various uses as modern advanced materials. There have been attractive studies on cellulosics directed toward elaborate designs of highly functionalized material systems for many-faceted prospective applications, via synthesis of this polysaccharide molecule itself,[1] precise derivatization,[2–4] mesoscopic self-assembly such as the formation of liquid crystals,[5] microscopic incorporation with other adequate polymeric or inorganic ingredients,[5] and material reinforcement by cellulosic nanofibrillar networks.[6, 7]

This work was partially financed by "Research Fund for Development of Technologies from Nature" from Sekisui Chemical Co., Ltd. and a Grant-in-Aid for Challenging Exploratory Research (No. 22658052) from the Japan Society for the Promotion of Science (JSPS).

Address correspondence to Yoshiyuki Nishio, Division of Forest and Biomaterials Science, Graduate School of Agriculture, Kyoto University, Kitashirakawa Oiwake-cho, Sakyo-ku, Kyoto 606-8502, Japan. E-mail: ynishio@kais.kyoto-u.ac.jp

Essentially, such concepts can contribute to modern functionalization of its parent substance, wood.

In this article, we would like to exemplify a successful production of thermally processible wood exhibiting a unique magnetic behavior. As an immediate background of the motivation, the design of magnetic nanocomposites based on cellulose and related polysaccharides has attracted considerable attention in the past two decades.[5, 8–13] The potential application includes information transfers or storage media, fabrics for electromagnetic shielding, new filtration and separation systems, and magnetic drug-delivery systems. A technique of interest for the compositions is *in-situ* synthesis[5, 8–13] of iron oxide nanoparticles in fibrillar suspensions or gels of polysaccharides, rather than physical loading of magnetic pigments into the polymer matrices. The standard of the chemical loading method consists of three steps: (1) ferrous ion-absorption of the original polymer materials following their swelling or gelation in a ferrous salt solution (typically aqueous $FeCl_2$ or $FeSO_4$); (2) *in-situ* precipitation of ferrous hydroxide by an alkaline treatment of the swollen polymers usually with aqueous hydroxide of alkali or alkali-earth metal; (3) oxidation of the ferrous hydroxide with an oxidizing agent (e.g. H_2O_2) or O_2-bubbling. A significant feature in the adoption of this chemical method is that the composite materials prepared can exhibit superparamagnetism (SPM); that is, there is no remanent magnetization (M_r) and coercive force (H_c) in magnetic hysteresis-loop measurements, in contrast to the common ferro(i)magnetism (FM). The unique magnetic character can be observed when the magnetic particles are dispersed in the matrix on a scale of less than a few tens of nanometers.

Previously, the authors' group prepared alginate-based magnetic gels by the above-stated procedure for *in-situ* synthesis of iron oxides.[5,13] An interpenetrating network (IPN) type of alginate/poly(vinyl alcohol) (PVA) gels containing iron oxide was also designed to acquire a variable viscoelastic property.[5,13] In the present work, originally intractable wood matter is employed as a fascinating matrix for the *in-situ* synthesis. To facilitate ferrous ion-absorption, we attempt hydrophilic/anionic functionalization of wood flour (WF) by hydroxypropylation and carboxymethylation; this combination of etherification is also expected to be favorable in improving thermoplasticity of the products. The purpose of this study is to demonstrate a fabrication of "see-through" thermoplastic woody magnetic sheet exhibiting an SPM character.

EXPERIMENTAL

Materials

The original WF material used was a commercial product of softwood (Norway Spruce) flour, Lignocel S150TR, with an average diameter of ~120 μm, was supplied by Rettenmaier Japan Co., Ltd. (Japan). The WF was extracted in a

Downloaded At: 11:56 25 January 2011

Soxhlet extractor with an ethanol/benzene solution (1/2 by volume) for 6 h, and dried at 40°C for 24 h *in vacuo*. All the chemicals and solvents used were reagent grades and used without further purification.

Etherification of WF

Hydroxypropylation and carboxymethylation of WF were carried out in accordance with the conventional etherification method for cellulose.[14] To a flask containing a sludge of WF (2 g), which was filtrated after immersion in distilled water for 24 h, 43 wt% aqueous NaOH solution (75 g) was added and vigorously stirred over a period of 4.5 h at room temperature under reduced pressure (~50 mmHg). The agitation was continued for 30 min in an ice bath under a nitrogen atmosphere, and then propylene oxide (50 mL) was added into the flask. With continuous stirring, the reaction mixture was heated to 50°C and kept in that temperature for 48 h. The reaction liquor was then neutralized with 1 M aqueous HCl solution and the fibrous hydroxypropylated WF product (HP-WF) was washed by dialysis. After centrifugation, the HP-WF was dried at 40°C *in vacuo*.

Thus obtained HP-WF was provided for the following carboxymethylation. A slurry of HP-WF (1.5 g) in 2-propanol (40 mL) was stirred vigorously in a flask while 30 wt% aqueous NaOH (4 mL) was added drop-wise during 10 min at room temperature. Stirring was continued for another 1 h; 4-mL solution of sodium monochloracetate (1.8 g) in isopropanol was then added dropwise and the flask was immersed in a water bath regulated at 55°C. With continued stirring, the flask was left in the bath for 3.5 h. Following that, the reaction liquor was drained from the fibrous product (CMHP-WF); the latter was stirred in 70 wt% aqueous methanol while sufficient 90 wt% acetic acid was added to neutralize the excess alkali. The product was drained, washed with 70 wt% methanol and then with absolute methanol, and finally dried *in vacuo* at 40°C.

Downloaded At: 11:56 25 January 2011

In-Situ Synthesis of Iron Oxide in Etherified WF Matrix

The procedures for *in-situ* synthesis of iron oxide in the woody matrix were carried out in an atmosphere of nitrogen except for an oxidizing step. First, CMHP-WF (0.2 g) was immersed in a 0.025 M $FeCl_2$ aqueous solution (~100 mL). After standing for 24 h at room temperature, the solid was centrifuged and washed with distilled water. The thoroughly washed ferrous CMHP-WF (Fe-CMHP-WF) was then steeped in an aqueous alkaline solution (~100 mL, pH $\approx$ 13) for 24 h. Subsequently, the system was heated to 65°C and 2 wt% hydrogen peroxide solution (~10 mL) was added thereinto dropwise over a period of ~15 min. The oxidized product was once washed with distilled water and dried *in vacuo* at 40°C. We repeated the series of procedure for the *in-situ* synthesis of iron oxide and obtained the objective product (o-Fe-CMHP-WF).

The iron content in the composite was determined by a reduction/oxidation titration method. Ferric ions were extracted from a weighed fragmental sample of the dried composite with a warmed HCl solution, then reduced to Fe^{2+} with the aid of tin(II) chloride. The ferrous ionic solution was titrated with potassium dichromate by using diphenylamine-4-sulfonate as an indicator.

Measurements

Fourier transform infrared (FTIR) spectra of the woody samples at each stage of modification were obtained by using a Shimadzu FTIR-8600 spectrometer. An ordinary KBr pellet method was adopted for all measurements.

Magnetometry measurements were carried out on 6-mg samples (freeze-dried) with a superconducting quantum interference device (SQUID), MPMS-5 of Quantum Design Inc. The magnetic field (H) was applied, usually varied as $0 \rightarrow 5\ \mathrm{T} \rightarrow -0.1\ \mathrm{T} \rightarrow 0$ at a constant temperature. Data of the magnetization (M) were collected at 298 and 100 K. For zero-field-cooled (ZFC) magnetization, the sample was cooled to 5 K with the magnetic field set at zero. After stabilization at 5 K for 30 min, a magnetic field of 0.01 T was applied, and the magnetization was measured. The measurements were done while the temperature was increased from 5 to 300 K at 20 K increments. The stabilization time for each temperature step was 30 s. Subsequently, field-cooled (FC) experiments was performed; the sample was cooled to 5 K with the magnetic field of 0.01 T, and the magnetization data were acquired every 20 K after holding at a prescribed temperature for 30 s.

Downloaded At: 11:56 25 January 2011

RESULTS AND DISCUSSION

The WF treated by the sequential etherification (hydroxypropylation and carboxymethylation) imparted a color of light-yellow. Weight recovery percentages were 106.3 wt% and 101.4 wt% after hydroxypropylation of WF and carboxymethylation of hydroxypropylated WF (HP-WF), respectively. These values do not directly reflect the respective degrees of etherification, since some molecules of hydroxypropylated and carboxymethylated polysaccharides may become water-soluble depending on the degrees of substitution and these may be eluted in the reaction and purification (dialysis, centrifugation, and washup) systems. After the process of chemical loading of iron oxide, the coloration changed into ruddy brown, which indicates a successful incorporation of iron oxide particles (synthetic ferrites) into the etherified WF matrix. Elution of the etherified WF in this process appeared to be less pronounced, because possible water-soluble parts had already been removed in the etherification steps. Redox titrimetry revealed that the iron content of the final product was to be ∼4.0 wt%.

Figure 1 illustrates FTIR spectra of (a) untreated WF, (b) HP-WF, (c) carboxymethylated HP-WF (CMHP-WF), and (d) the final product (o-Fe-CMHP-WF) containing iron oxide. In contrast to the situation of the original WF,

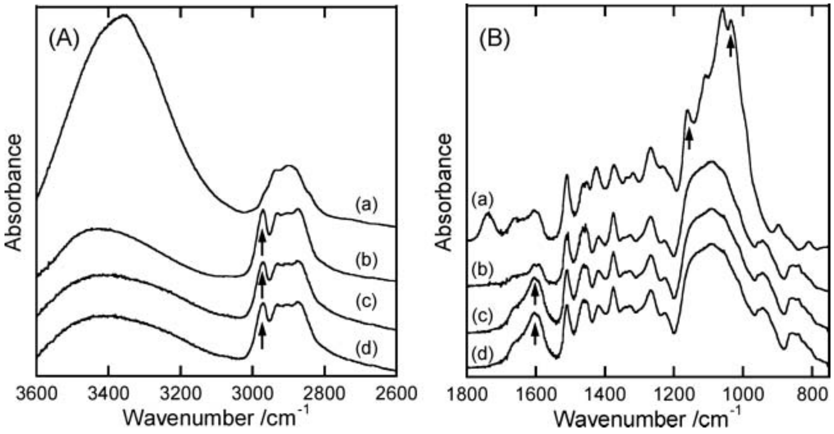


Figure 1. FTIR spectra of (a) WF, (b) HP-WF, (c) CMHP-WF, and (d) o-Fe-CMHP-WF, represented for the wavenumber regions of (A) 2600–3600 cm^{-1} and (B) 750–1800 cm^{-1}.

a drastic depression was observed in the spectral region associated with OH stretching (~3400 cm^{-1}) for the etherified products, which implies a decrease in the relative content of hydroxyl groups. Instead, a new characteristic absorption signal appeared at 2970 cm^{-1} in the FT-IR spectra of the other three (b)–(d), corresponding to a C—H (CH_3) stretching vibration. It is evident from the three data that the methyl group was introduced into WF in the hydroxypropylation step. In addition, two sharp absorption bands at 1030 and 1160 cm^{-1}, which can be attributed to ν_{C-O} of C2/C3—OH and C6—OH, respectively,[15] of the cellulose component of WF, became less prominent; this implies that the original cellulosic OH-groups were considerably substituted by hydroxypropyl moiety. The present etherification conditions including the following carboxymethylation are supposed to have modified the other two components of wood, hemicellulose, and lignin, too,[16] but the detailed analysis has not yet been accomplished. After carboxymethylation, the FTIR spectra contained a larger absorption band assigned as a symmetric stretching vibration of the carboxylate moiety, at 1605 cm^{-1}. It should be noted, however, that the carboxymethylation gave rise to less variation in IR spectrum, relative to the after-effect of the hydroxypropylation, which indicates that the degree of the carboxymethyl modification was rather modest. On the other hand, no appreciable difference was detectable in the spectra between before and after the *in-situ* synthesis of iron oxide, as can be seen from comparison of data (d) with (c) in Figure 1.

By means of the set of etherification, the original WF was converted into a thermoplastic material. Actually it was possible to mold the modified WF samples into a film form at a relatively low temperature of 180°C, even after the

Downloaded At: 11:56 25 January 2011

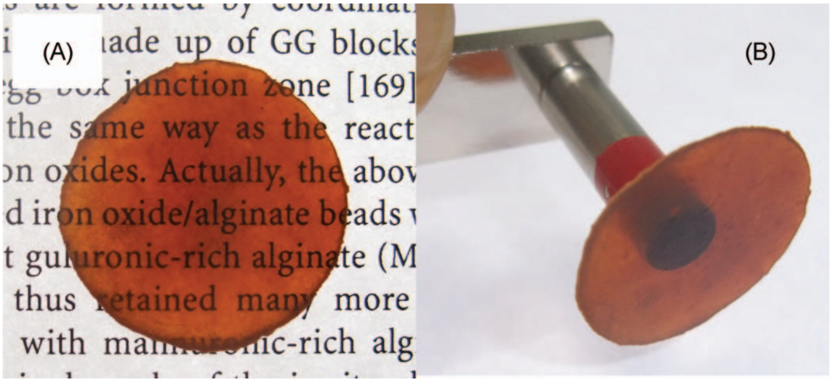


Figure 2. Visual appearance of a hot-pressed o-Fe-CMHP-WF film sheet transparent under an interior light (part A) and responsive to a bar magnet (part B).

Downloaded At: 11:56 25 January 2011

in-situ synthesis of iron oxide. As demonstrated in Figure 2, the molded sheet was transparent and homogeneous visually, and responsive to a bar magnet.

Quantitative magnetometry measurements were conducted for the hot-pressed o-Fe-CMHP-WF sheet. Figure 3 illustrates the magnetization behavior at 100 and 298 K as a function of externally applied magnetic field (H). The magnetization (M) data obtained at 298 K exhibited a characteristic M versus H profile in which a steep rise of magnetization occurred and there appeared no remanent magnetization. Then the magnetism can be regarded as SPM, which is usually observed when the magnetic particles are dispersed in the matrix in a scale of less than a few tens of nanometers.

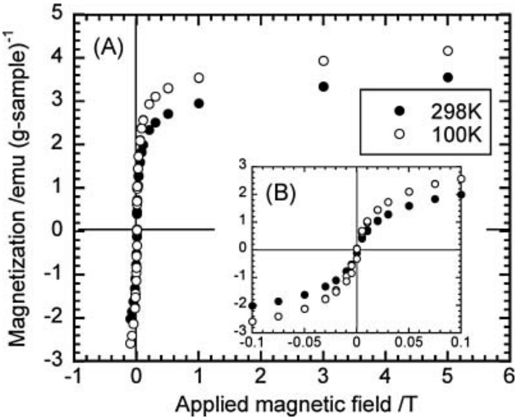


Figure 3. Magnetization versus H-field curves for a thermally molded o-Fe-CMHP-WF sheet, measured at 100 and 298 K. (B) shows the data on an enlarged scale.

Downloaded At: 11:56 25 January 2011

By regression of the magnetization data in a range of 0–5 T, a saturation magnetization (M_s) was determined in terms of the following classical Langevin function[17]:

$$M = M_s[\coth(\alpha) - \alpha^{-1}]$$

with $\alpha = \mu H/k_B T$, where μ is a magnetic moment per particle, k_B is the Boltzman constant, and T denotes absolute temperature. M_s at 298 K was determined to be 3.11 emu (g-sample)$^{-1}$; this value being considerably larger than those estimated for the alginate/PVA IPNs showing a similar magnetism.[13]

With regard to the temperature dependence of the magnetization behavior, the magnetism at 100 K could be judged to be pseudo SPM character, but, strictly, the M-H curve provided a very slight hysteresis loop with nonzero values of remanent magnetization and coercive force. The hysteric behavior is a sign of FM, related to the magnetic anisotropy. In general, the SPM to FM transition is correlated to a blocking phenomenon,[17] in which the magnetic moments of the particles considered are frozen along their anisotropy axes. The transition temperature (T_B) should shift depending on the distribution of the particle radius of gyration, lowered with a decrease in the size of the particle. A commonly used technique for determination of the transition temperature is to examine the field-cooled (FC) and zero-field-cooled (ZFC) magnetizations, that is, the magnetizations followed as a function of temperature after the sample has been cooled, respectively, in the presence and absence of a weak magnetic field. Figure 4 shows FC and ZFC data obtained for the o-Fe-CMHP-WF sheet

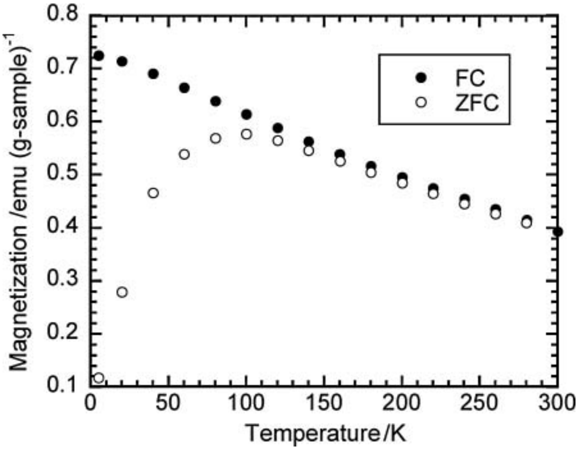


Figure 4. Temperature dependence of the magnetization in a field of 0.01 T for a thermally molded o-Fe-CMHP-WF sheet. The FC and ZFC curves were obtained for the sample with and without the field prior to the measurements, respectively.

in a magnetic field of 0.01 T. At high temperatures, the set of data exhibited the same trend, however, at lower temperatures the data significantly diverged. The ZFC curve passed through a maximum at 100 K ($T_{\max}$). $T_{\max}$ is related to T_B by the following equation:

$$T_{\max} = \beta T_B$$

where the β value changes with the size distribution of the magnetic particles.[18, 19] For the particles with size distributions, β is typically in the range of 1.5–2.0.[18, 19] Actually, the broadness of the peak maximum of the ZFC curve reflects that the iron oxide nanoparticles in the WF matrix were polydisperse in size. Thus T_B was estimated to be in the temperature region of 50–67 K. It can therefore be assumed for the o-Fe-CMHP-WF composite concerned that the dimensions of the magnetic particles dispersed in were too minute to give rise to a clear transition in the temperature range of $\geq$ 100 K.

Downloaded At: 11:56 25 January 2011

CONCLUSIONS

It was thus found that WF could be converted not only to a thermoplastic material but also to a carrier matrix for the *in-situ* synthesis of iron oxide nanoparticles by the set of etherification, namely by a good deal of hydroxypropylation and successive modest carboxymethylation. The present success allows us to design diverse applications of new light-weight woody magnetic materials that are furnished with a thermal processibility, transparency, and availability for nailing/tacking. Besides, the observation of SPM may be of significance in the perceptibility to an external magnetic stimulus only on demand and without energy loss. One possible application is a large magnetic panel; we do not have to be nervous about some undesirable effects of magnetic fields due to remanent magnetization. Further work on the optimization of chemical modification of wood is in progress, in parallel with a more detailed characterization of the size and morphology of the magnetic particles by microscopy and diffractometry.

REFERENCES

1. Nakatsubo, F.; Kamitakahara, H.; Hori, M. Cationic ring-opening polymerization of 3,6-di-O-benzyl-α-D-glucose 1,2,4-orthopivalate and the first chemical synthesis of cellulose. J. Am. Chem. Soc. **1996**, *118* (7), 1677–1681.
2. Isogai, A.; Kato, Y. Preparation of polyglucuronic acid from cellulose by TEMPO-mediated oxidation. Cellulose **1998**, *5* (3), 153–164.
3. Klemm, D.; Heublein, B.; Fink, H.P.; Bohn, A. Cellulose: Fascinating biopolymer and sustainable raw material. Angew. Chem. Int. Ed. **2005**, *44* (22), 3358–3393.

Downloaded At: 11:56 25 January 2011

4. Sakakibara, K.; Ogawa, Y.; Nakatsubo, F. First cellulose Langmuir-Blodgett films towards photocurrent generation systems. Macromol. Rapid Commun. **2007**, *28* (11), 1270–1275.
5. Nishio, Y. Material functionalization of cellulose and related polysaccharides via diverse microcompositions. Adv. Polym. Sci. **2006**, *205*, 97–151.
6. Samir, M.A.S.A.; Alloin, F.; Dufresne, A. Review of recent research into cellulosic whiskers, their properties and their application in nanocomposite field. Biomacromolecules **2005**, *6* (2), 612–626.
7. Yano, H.; Sugiyama, J.; Nakagaito, A.N.; Nogi, M.; Matsuura, T.; Hikita, M.; Handa, K. Optically transparent composites reinforced with networks of bacterial nanofibers. Adv. Mater. **2005**, *17* (2), 153–155.
8. Marchessault, R.H.; Ricard, S.; Rioux, P. *In situ* synthesis of ferrites in lignocellulosics. Carbohydr. Res. **1992**, *224*, 133–139.
9. Marchessault, R.H.; Rioux, P.; Raymond, L. Magnetic cellulose fibres and paper: preparation, processing and properties. Polymer **1992**, *33* (19), 4024–4028.
10. Ziolo, R.F.; Giannelis, E.P.; Weinstein, B.A.; Ohoro, M.P.; Ganguly, B.N.; Mehrotra, V.; Russell, M.W.; Huffman, D.R. Matrix-mediated synthesis of nanocrystalline γ-Fe_2O_3: A new optically transparent magnetic material. Science **1992**, *257* (5067), 219–223.
11. Raymond, L.; Revol, J.F.; Marchessault, R.H.; Ryan, D.H. *In situ* synthesis of ferrites in ionic and neutral cellulose gels. Polymer **1995**, *36* (26), 5035–5043.
12. Kroll, E.; Winnik, F.M.; Ziolo, R.F. In situ preparation of nanocrystalline γ-Fe_2O_3 in iron(II) cross-linked alginate gels. Chem. Mater. **1996**, *8* (8), 1594–1597.
13. Nishio, Y.; Yamada, A.; Ezaki, K.; Miyashita, Y.; Furukawa, H.; Horie, K. Preparation and magnetometric characterization of iron oxide-containing alginate/poly(vinyl alcohol) networks. Polymer **2004**, *45* (21), 7129–7136.
14. Whistler, R.L., Ed. *Methods in Carbohydrate Chemistry III*; Academic Press: New York and London, 1963.
15. Langkilde, F.W.; Svantesson, A. Identification of celluloses with Fourier-transform (FT) mid-infrared, FT-Raman and near-infrared spectrometry. J. Pharm. Biomed. Anal. **1995**, *13* (4/5), 409–414.
16. Rowell, R.M. Chemical modification of wood. In *Wood and Cellulosic Chemistry*; Hon, D.N.S., Shiraishi, N., Eds.; Marcel Dekker, Inc.; New York, 1991; 703–756.
17. Cullity, B.D.; Graham, C.D., Eds. *Introduction to Magnetic Materials*; 2nd ed.; Wiley: Hoboken, New Jersey, 2009.
18. Gittleman, J.I.; Abeles, B.; Bozoeski, S. Superparamagnetism and relaxation effects in granular Ni-SiO_2 and Ni-Al_2O_3 films. Phys. Rev. B **1974**, *9* (9), 3891–3897.
19. Tang, B.Z.; Geng, Y.; Lam, J.W.Y.; Li, B.; Jing, X.; Wang, X.; Wang, F.; Pakhomov, A.B.; Zhang, X.X. Processible nanostructured materials with electrical conductivity and magnetic susceptibility: Preparation and properties of maghemite/polyaniline nanocomposite films. Chem. Mater. **1999**, *11* (6), 1581–1589.