

FABRICATING UNIDIRECTIONAL MAGNETIC PAPERS USING PERMANENT MAGNETS TO ALIGN MAGNETIC NANOPARTICLE COVERED NATURAL CELLULOSE FIBERS

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This paper reports a simple innovative method to align magnetic cellulose fibers by using a simple permanent magnet to fabricate unidirectional magnetic papers. Magnetic cellulose fibers were made by in situ synthesis of magnetite nanoparticles on alpha cellulose pulp extracted from American southern pine. Scanning electron microscope micrographs and energy dispersive X-ray spectroscopy maps indicated that magnetite nanoparticles completely covered the cellulose fibers. Suspensions of magnetic cellulose fibers were prepared at three levels of concentration (0.02, 0.04, and 0.08 g/L) and poured into the designed magnetic forming machine. Flow rate of suspension into the forming column was adjusted at 0, 0.3, 0.5, and 1 cm/s. The strength of the applied external magnetic field was the same in all cases and lower than 0.18 T. Orientation analysis indicated that the designed magnetic forming machine has a high performance to be used for aligning magnetic cellulose fibers and fabricating unidirectional magnetic cellulose papers. Observed anisotropic magnetic and mechanical properties confirmed the unidirectional structure.

Keywords: Unidirectional magnetic paper; Magnetic alignment; Magnetic nanoparticle; Magnetic cellulose fiber; Permanent magnet

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INTRODUCTION

Although magnetism and magnetic materials have been well known for many years, it is only recently that a number of new techniques to provide more sophisticated methods of material processing have been developed (Kimura and Kimura 2008). Different materials respond differently to externally applied magnetic fields depending on their nature and structures. Cellulose is well known as the most abundant biopolymer on Earth (Kim et al. 2008). It has been demonstrated that anisotropic natural cellulose fibers show negative diamagnetic behavior intrinsically when affected by external strong magnetic fields and can align perpendicular to the applied magnetic field direction. Because the diamagnetic property is a feeble magnetic behavior, the externally applied magnetic field must be strong enough, up to about 20 T, to provide sufficient torque to align the cellulose fibers perpendicular to the magnetic field direction efficiently (Revol et al. 1994; Kimura et al. 2005; Fujimura et al. 2010; Sundar et al. 2011). Producing such

strong magnetic fields needs special superconducting magnets that are characterized as expensive and high technologies. There are a few countries in the world having the technical knowledge required to make superconducting magnets. Moreover, high investment to produce superconducting magnets, costs of their energy consumption, safe keeping, and the need for servicing are additional disadvantages. All these mentioned problems limit using superconducting magnets to some specialized magnetic materials laboratories. There are several successful reports on aligning cellulose fibers at both micro and nanoscales by using superconducting magnets (Sugiyama et al. 1992; Kimura et al. 2005; Kimura and Kimura 2008; Fujimura et al. 2010; Li et al. 2010). On the other hand, during the last decades, some researchers have focused on using cellulose fibers as substrates to keep or synthesize magnetic particles. Reportedly, there are two major methods for fabricating magnetic natural cellulose fibers (Marchessault et al. 1992; Chia et al. 2008; Small and Johnston 2009; Chia et al. 2009; Matsumoto et al. 2010; Wu et al. 2011): lumen loading of natural cellulose fibers with micro-scale conventional magnetic pigments, and the other, using nanoporosities of the surfaces of natural cellulose fibers as nanoreactors for the *in situ synthesis* of magnetic nanoparticles on cellulose fibers. The fabricated magnetic cellulose fibers show strong magnetic properties in comparison to the weak magnetic properties of the starting raw cellulose fibers. Also, these fabricated magnetic cellulose fibers have been used to make magnetic cellulose papers. Magnetic papers have potential applications in production of information storage devices, security cards, electromagnetic shields, and so forth (Marchessault et al. 1992; Chia et al. 2008).

This paper presents a novel method to process and fabricate unidirectional magnetic cellulose papers by using interactions of magnetic cellulose fibers in suspension with externally applied magnetic field generated from a simple permanent magnet. Based on our review of the literature, this is the first report on fabricating unidirectional magnetic papers by using simple permanent magnets. We believe this method provides a quite simple and inexpensive way to efficiently align magnetic cellulose fibers and fabricate unidirectional magnetic papers. These unidirectional magnetic papers showed anisotropic physical and mechanical behaviors and have the potential to be used in fabricating a new class of anisotropic magnetic composites. These anisotropic magnetic papers present magnetism, flexibility, strength, and stiffness anisotropy, making them potentially suitable to be used for advanced new materials where different behaviors in different planes or directions are desired. Possible applications include but are not limited to lightweight magnetic actuators and micro robots.

EXPERIMENTAL

Materials and Processing

Magnetic cellulose fibers were prepared by *in situ synthesis* of magnetite nanoparticles on conventional alpha cellulose pulp extracted from American southern pine (Linter Pack Co, Iran). To fabricate magnetic cellulose fibers, *in situ synthesis* of magnetite nanoparticles in optimal condition as reported by Long et al. (2009) was used. *In situ synthesis* of magnetite nanoparticles was performed by adding NaOH (Nacalai Tesque, Japan) and oxidation of water suspension of cellulose fibers and two hydrous

iron salts, $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ and $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ (Nacalai Tesque, Japan) at 60°C under vigorous magnetic stirring (1000 rpm) and constant flow of argon gas to eliminate the unwanted oxidation before desirable time. The fabricated hybrid magnetic cellulose fibers (HMCFs) were then washed with a lot of tap water to remove surplus magnetic nanoparticles.

Figure 1 shows a schematic of the designed machine to magnetically align HMCFs for fabricating unidirectional magnetic paper sheets (UMPSs). This simple machine provides the possibility to control some important forming factors affecting alignment quality of HMCFs in the final structure of UMPSs. Modulated external magnetic field was provided by a simple permanent magnet. Figures 1g and 1h illustrate the magnetic gradient at forming wire net. Concentration of magnetic fibers in the suspension at 3 levels (0.02, 0.04 and 0.08 g/L) and average flow rate of HMCFs at 4 levels (0, 0.3, 0.5, and 1 cm/s) were investigated to find the optimal condition for achieving to the best alignment.

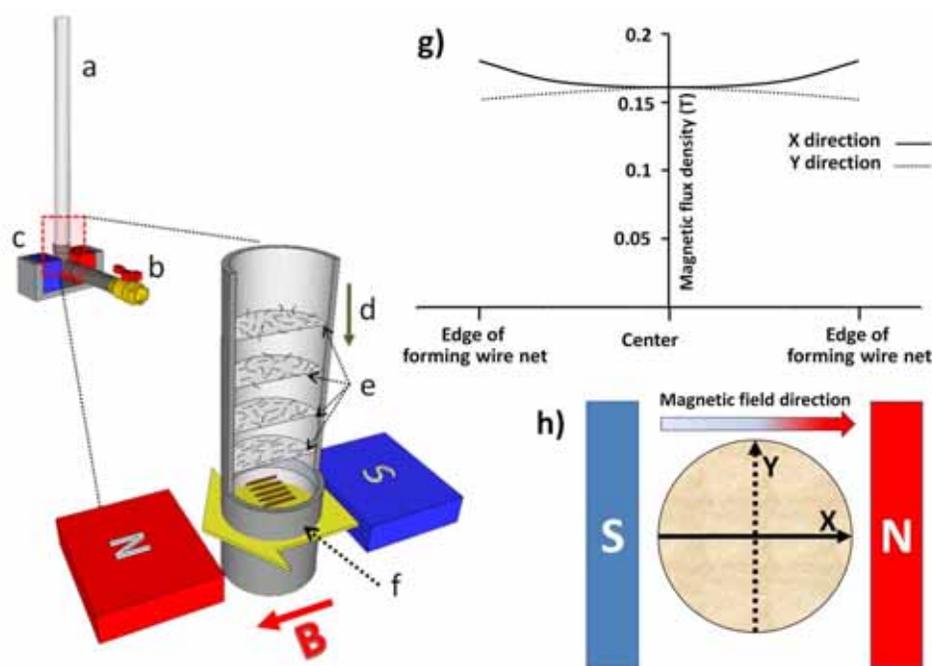


Fig.1. Detailed schematic of the designed magnetic forming machine: a) transparent poly-acrylic pipe (forming column), b) special valve for adjustment suspension flow, c) permanent magnet, d) gradual flowing or settling down of HMCFs, e) hypothetical horizontal plates, f) location of forming wire net, g) gradient of magnetic flux density between two poles, h) schematic guide of the mentioned X and Y directions used to evaluate flux density gradient.

Detection and Characterization

A number of methods were used to characterize the magnetic cellulose fibers and investigate orientation distribution in the fabricated magnetically aligned magnetic paper sheets. The natural cellulose fibers coated with magnetite nanoparticles were observed by a field emission scanning electron microscope (FE-SEM, Hitachi S-4800, Hitachi Science System Ltd., Japan). The accelerating voltage applied was 1.5 kV, and the surfaces of samples were sputter coated with platinum. X-ray diffraction (XRD) measurements were

carried out using a Rigaku Ultima-IV diffractometer with Cu K α radiation in 2θ range from 5 to 70. The accelerating voltage and current were 40 kV and 40 mA, respectively. Energy dispersive X-ray spectroscopy (EDS) was performed on an EDAX instrument (Genesis XM2, USA) set on the FE-SEM S-4800. The accelerating voltage and working distance were 20 kV and 15 mm, respectively. To investigate the magnetic alignment of HMCFs in the final fabricated magnetic paper sheets under different conditions, a digital microscope camera (VH-Z500R, Keyence Co. Japan) was used to take 2D images from the surface alignment. The acquired images were then analyzed by OrientationJ, a specialized plugin of ImageJ software (National Institutes of Health, USA) developed by Biomedical Imaging Group (BIG) from Lausanne, Switzerland. Measurements of static tensile strength were performed using a Tensiometer FGP-50 (Nidec-Shimpo Corporation, Japan). For tensile measurement, samples were cut to dimensions of 5 mm wide and 20 mm long. The gauge length and cross head speed were 10 mm and 10 mm/min, respectively.

RESULTS AND DISCUSSION

From FE-SEM micrographs, successfully produced *in situ synthesized* magnetite nanoparticles can be clearly seen (Fig. 2, A). These micrographs indicate that the synthesized nanoparticles completely covered the individual cellulose fibers. X-ray diffraction (XRD) patterns of the HMCFs displayed distinct peaks at 2θ values of about 18.2, 30.1, 35.3, 42.9, 53.2, 57.1, and 62.6, corresponding to the characteristic peaks of magnetite (Fig. 2, B) (Small and Johnston 2009). Also, the detected strong peaks at around 15.7, 22.5, and 34 were related to the cellulose type-I. Average crystalline size of the *in situ synthesized* magnetite nanoparticles were calculated from FWHM (full width at half-maximum intensity) by using the Scherrer's equation, expressed as $D = 0.89 \lambda / \beta \cos \theta$, where λ is the wavelength (Cu K α), β is FWHM of magnetite XRD peak at 35.3 (311), and θ is the Bragg angle of diffraction peak (311). The average size of magnetite nanoparticles was determined to be around 6 nm.

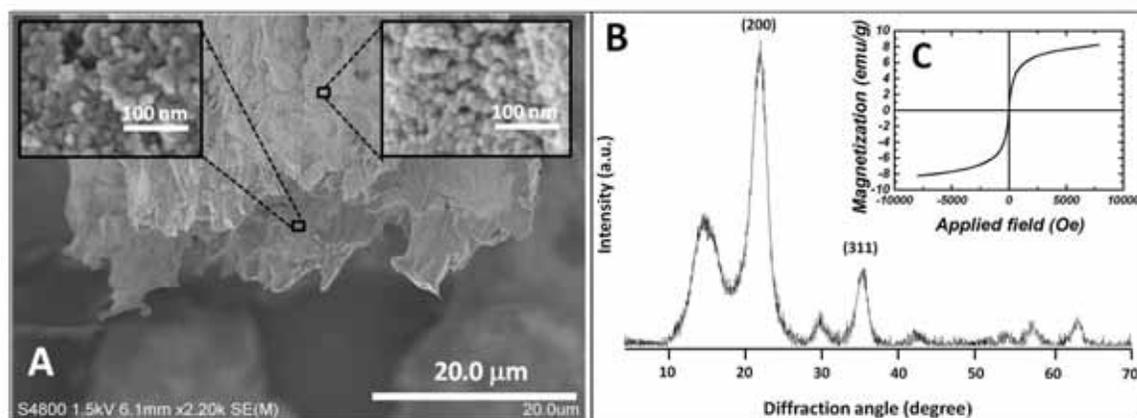


Fig. 2. A) FE-SEM micrographs of HMCFs, B) X-ray diffraction profile of HMCFs, and C) magnetization of HMCFs

The difference between findings from FE-SEM and XRD could be due to the aggregation phenomenon of the fine magnetite nanoparticles and formation of larger spherical magnetite nanoparticles (Xuan et al. 2009). Figure 2, C shows magnetization behavior of magnetic cellulose fibers evaluated by the vibrating sample magnetometer. Because there were no remanence and coercivity, it is suggested that the fabricated magnetic cellulose fibers were superparamagnetic (Fig. 2, C).

The appearance of Fe on the surface of HMCFs was traced by examining the EDS map for Fe (Fig. 3). The EDS map confirmed that the magnetite nanoparticles densely covered the cellulose fibers. It seemed that these HMCFs could be used to align and fabricate unidirectional magnetic papers if exposed to a strong enough external magnetic field under suitable conditions. Therefore, the magnetic forming machine was designed and made to fabricate the unidirectional magnetic papers from suspensions.

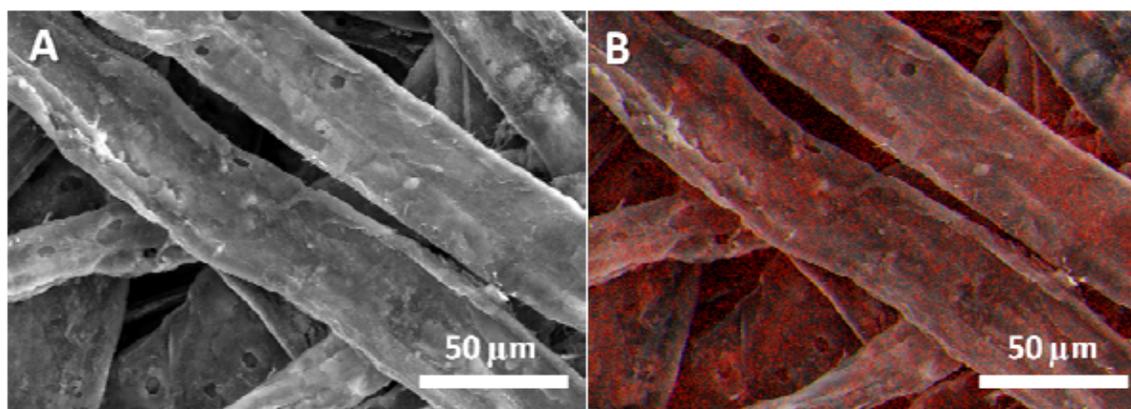


Fig. 3. EDS images of HMCFs, A) complementary SEM image and B) elemental Fe map

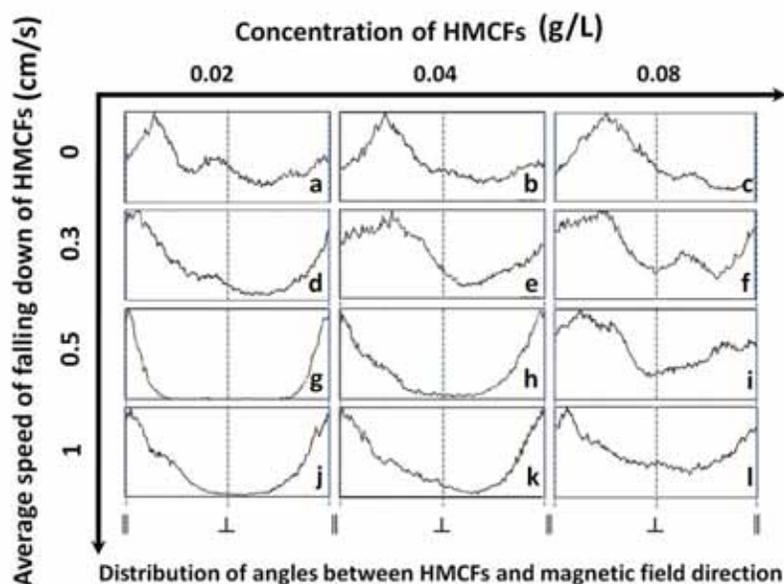


Fig. 4. Profiles of magnetic alignment distributions of HMCFs in different conditions

Figure 4 shows the effects of changes in the concentration levels of magnetic fibres in suspension and average flow rate of magnetic cellulose fibers on the quality of alignment of HMCFs. The flow rate of 0.15 cm/s is the average actual flow rate of individual magnetic cellulose fibers, while the flow rate of suspension is 0 cm/s when the control valve is closed and the hybrid magnetic fibers deposit only under gravity. To determine the average actual flow rate of individual HMCFs, the actual flow rates were measured for about 50 randomly selected magnetic cellulose fibers in a 30 cm distance when the flow rate of the suspension was 0 cm/s.

Image analysis indicated that alignment qualities were not satisfactory when the flow rate was around 0 cm/s. Increasing the concentration level of the HMCFs from 0.02 to 0.08 g/L increasingly worsened the alignment quality. Magnetic cellulose fibers geometries are not same because naturally, structural fibers of trees are different from each other. This may result in different deposition rates for different fibers. When these fibers fall down solely affected by gravity, larger fibers pass the height of the forming column more quickly and during this time they can contact with the other floating fibers and make bulky structures. Since these structures are formed from randomly aligned assembled magnetic cellulose fibers, they have almost isotropic structures and they sit on the forming wire screen without any special orientation. On the other hand, because the interlocked magnetic fibers are heavier than individual fibers, they travel faster depending on the number and size of the randomly aligned interlocked fibers resulting in increased bulk sizes, while the structures move down gradually (Fig. 5, A-B).

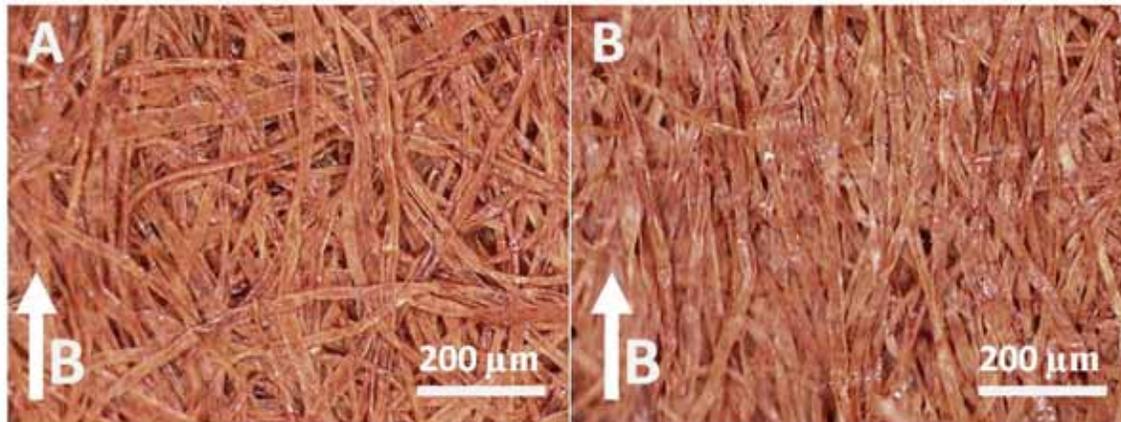


Fig. 5. Digital microscope camera photograph of A) randomly aligned and B) unidirectionally aligned magnetic cellulose fibers

Generally, reducing the concentration of magnetic cellulose fibers in suspension increased the quality of magnetic alignment due to increasing free space for each individual fiber to move down and rotate freely without connecting to other fibers and forming massive and large bulky structures of interlocked fibers. On the other hand, increase or decrease in the flow rate of the suspension with adjusting the control valve and thereby adjusting magnetic fibers deposition speed, seems to have achieved an optimal condition. If the flow rate is very low, bulky structures form, and if the speed is too high, the required time for the alignment of each individual magnetic fiber is not

sufficient and the final efficiency will decrease. In this study, according to the results, the best quality of alignment was achieved at the concentration level of 0.02 g/L and flow rate of 0.5 cm/s. It seems that in this condition each individual HMCF has sufficient free space and time to align itself efficiently. Figure 6, A and B indicate the achievement of anisotropic magnetic and mechanical properties of the final fabricated unidirectional magnetic papers, respectively. The anisotropic response to an external magnetic field indicated the high quality of magnetic alignment and unidirectional structure of the fabricated magnetic papers. Anisotropic mechanical response was further evidence that the magnetic cellulose papers were made from efficiently aligned magnetic fiber components.

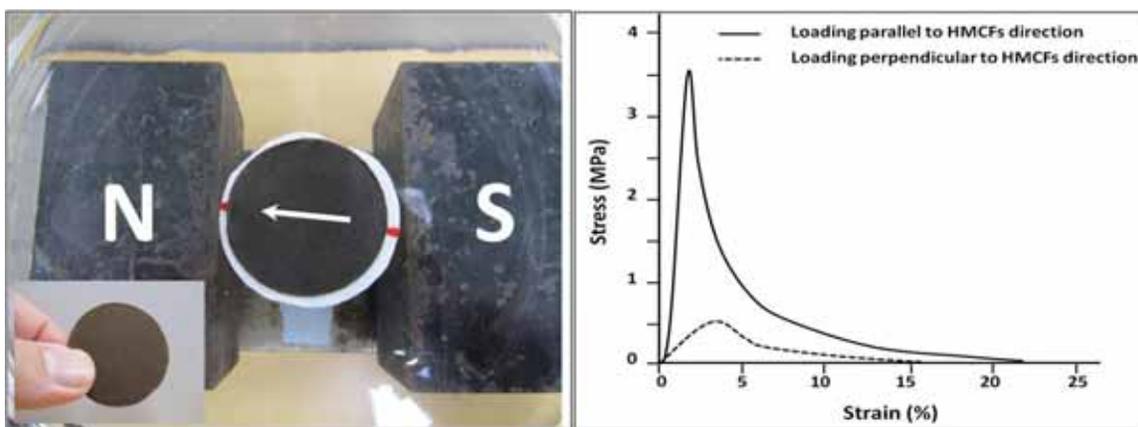


Fig. 6. A) Magnetic anisotropy of the unidirectional magnetic papers, white arrow shows alignment direction of HMCFs, B) typical stress-strain curves of the unidirectional magnetic papers

CONCLUSIONS

This paper presents a novel method to fabricate unidirectional magnetic papers from natural cellulose fibers coated with *in situ* synthesized magnetic nanoparticles using an externally applied magnetic field generated by a simple permanent magnet. The results showed that controlling the flow rate and concentration levels of magnetic cellulose fibers in suspension significantly affected the quality of magnetic alignment. The best results were achieved at the concentration level of 0.02 g/L and average deposition rate of 0.5 cm/s. The fabricated unidirectional magnetic papers showed anisotropic mechanical and magnetic properties.

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