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ORIGINAL PAPER

Magnetic alignment of cellulose nanowhiskers in an all-cellulose composite

Dongsheng Li · Zuyan Liu · Marwan Al-Haik · Mehran Tehrani · Frank Murray · Rina Tannenbaum · Hamid Garmestani

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Abstract Unidirectional reinforced nanocomposite paper was fabricated from cellulose nanowhiskers and wood pulp under an externally applied magnetic field. A 1.2 Tesla magnetic field was applied in order to align the nanowhiskers in the pulp as it was being formed into a sheet of paper. The magnetic alignment was driven by the characteristic negative diamagnetic anisotropy of the cellulose nanowhiskers. ESEM micrographs demonstrated unidirectional alignment of the nanowhiskers in the all-cellulose composite paper. Comparing with control paper sheets made from wood pulp only, the storage modulus in the all-cellulose nanocomposites increased dramatically. The storage modulus along the direction perpendicular to the magnetic field was much stronger than that parallel to the magnetic field. This new nanocomposite, which contains preferentially oriented microstructures and has improved mechanical properties, demonstrates the possibility of expanding the functionality of paper products and constitutes a promising alternative to hydrocarbon based materials and fibers.

Keywords Cellulose nanowhiskers · Unidirectional · Magnetic alignment · Nanocomposite · All-cellulose

D. Li (✉)
Fundamental and Computational Sciences Directorate, Pacific Northwest National Laboratory, Richland, WA 99352, USA
e-mail: dongsheng.li@pnl.gov

Z. Liu · R. Tannenbaum · H. Garmestani
School of Materials Science and Engineering, Georgia Institute of Technology, Atlanta, GA 30332-0245, USA

M. Al-Haik · M. Tehrani
Department of Engineer Science and Mechanics, Virginia Polytechnic Institute and State University, 225 Norris Hall, Blacksburg, VA 24061, USA

F. Murray
Institute of Paper Science and Technology, 500 10th St, Atlanta, GA 30332-0620, USA

Introduction

The past decade witnessed an exponential growth of the interest in cellulose-based materials. This is largely due to the increased awareness among consumers and engineers for sustainability. Cellulose, a renewable and abundant biopolymer and having an excellent mechanical performance at comparably low weight, naturally attracts investment of research and development. This trend is fueled particularly by the paper, forest, and textile industries, which are constantly searching for the development of value-added products that could compete with other high-tech industries [1].

Strong interest has been devoted in recent years to the properties and utilization of cellulose nanowhiskers, crystalline cellulose particles in nanoscale dimensions with aspect ratios in the range of 30–100, depending on their source. Cellulose nanowhiskers are manufactured from renewable materials such as natural plants, bacteria, fungi, algae, and marine animals. Even byproducts in the forest, agriculture, and paper industries may be employed as abundant, inexpensive, and readily available sources for cellulose nanowhiskers [2, 3]. For example, straw and other agriculture residues existing in the waste streams from commercial crop processing plant have traditionally constituted a disposal problem but may be an excellent source of cellulose nanowhiskers. Cellulose nanowhiskers are extracted from a purified cellulose source material by hydrolytic degradation, typically with a strong mineral acid such as sulfuric acid. The acid hydrolysis process initially produces micro-crystalline cellulose of predominantly coarse particulate aggregates, typically having a mean size range of about 15–40 microns. Further acid hydrolysis yields the desired nanoparticles. Microstructure characterization of cellulose nanowhiskers manufactured from different sources is listed in Table 1.

Cellulose nanowhiskers have excellent mechanical properties. The elastic modulus of the cellulose I crystallite, the major composition of nanowhisker and also the typical form from plant fibers, is around 130 GPa and strength of the order of 10 GPa [4, 5]. Table 2 compares the mechanical properties of cellulose nanowhiskers with their source materials and some structural materials. Moreover, cellulose nanowhiskers are quite affordable and easy to fabricate, especially as compared to other rod-like nanoparticles with similar mechanical properties, such as multi-walled carbon nanotubes. For example, the acid hydrolysis to fabricate cellulose nanowhiskers using a sulfuric acid concentration of 63.5% within 2 h

Table 1 Microstructure properties of cellulose nanowhiskers from different sources

Source	Size	Aspect ratio
Wood	1–5 nm width, 100-200 nm length	70
Cotton	1–5 nm width, 100 nm length	20
Seaweeds	5–20 nm width, 1–2 μm length	>100
Bacterial	8 nm width, 300 nm length	40
Filter paper	10 nm width, 300 nm length	30
Tunicate	10–20 nm diameter, 1–2 μm length	100

Table 2 Mechanical properties of cellulose nanowhiskers, their sources and other structural materials

Materials	Young's modulus (GPa)	Tensile strength (GPa)
Cellulose nanowhiskers	130	10
Wood	10–40	1
Cotton	5–13	0.3
Paper	7	0.1
Glass	70	2–3.5
Polyethylenes (HDPE)	0.8–1.0	0.015–0.045
Steel (AISI 1006)	200	0.3

came with a yield of 30% [6]. Availability and affordability make it possible and profitable to apply cellulose nanowhiskers on a large scale.

To take advantage of their excellent mechanical properties, cellulose nanowhiskers have been applied as a reinforcement additive in thermoplastic polymer composites [7–9]. However, the strength of polymer composites reinforced with cellulose nanocrystals remains far below what could be expected from their theoretical properties. This is due to the limited compatibility between the hydrophilic cellulose nanocrystals and the more hydrophobic polymer matrices. Poor dispersion of the nanowhiskers and the insufficient adhesion between the cellulose nanocrystals and the matrix induces unsatisfactory mechanical properties of the composites.

Compared with the intensive research work on thermoplastic polymer composites, there has been little study in producing all-cellulose composites comprised of pulp reinforced with nanowhiskers [10]. Since the chemical structures of the major constituents of pulp and cellulose nanowhiskers are the same, the compatibility of the matrix and the filler in this composite will not be an issue. Hence, it is expected that such an all-cellulose nanocomposite will exhibit a dramatic enhancement of mechanical properties.

As is evident in naturally occurring composites, the orientation and alignment of the reinforcing phase (the nanowhiskers and crystalline cellulose microfibers) in the composite matrix is a key feature responsible for the improved properties of the final paper product. The natural morphology and structure in straw and wood exhibits strong preferred orientation of cellulose along the growth direction [2]. Cellulose nanowhiskers have been reportedly oriented by various methods, such as magnetic fields [11–15], shearing forces [16], and electric fields [17]. Of these three externally applied forces, orienting the nanowhiskers under a shear force or an electric field has limited suitability for large scale production. For shear force orientation technology, it would be difficult to fabricate paper in large quantity via a batch process consisting of rotating concentric cylinders, and generating a continuous process using parallel plates would require a very large path that may be difficult to construct and maintain. For orientation via an electrical field technology, an apolar solution must be used. However, this alone would make the process prohibitive to the paper industry because of issues related to recycling, environmental protection, and cost. Unlike these two alignment methods, the use of an externally applied magnetic field may render itself suitable for large scale production, provided that a weak magnetic field

would be sufficient to align a large fraction of the cellulose nanowhiskers during paper casting. In this study, we investigated how an anisotropic, all-cellulose nanocomposite is fabricated under an externally applied magnetic field.

Experimental

Materials

Cellulose nanowhiskers were fabricated from microcrystalline cellulose by acid hydrolysis in 60% H_2SO_4 for 2 h at 55 °C. The solid residue was purified and refined by repeated cycles of 30 min of ultra centrifuging at 10,000 rpm and re-suspension of the solid in distilled water by ultrasonic mixing. After the turbid supernatant was obtained, the suspension was repeatedly dialyzed in distilled water until a pH of 5–6 was reached. 5 mL of 1% nanowhisker suspension was mixed with 19 mL of 5% fir pulp by sonication for 30 min. The mixture was vacuum filtered through filter paper in a magnetic field of 1.2 Tesla. Paper sheets were obtained by using slight compression to squeeze out the water and drying at 100 °C for 15 min.

Environmental scanning electronic microscopy (ESEM)

The microstructure observation was carried out using an Electroscan model E-3 ESEM to avoid surface destruction and charging. No metal or carbon coating was used to improve conductivity since it could distort the surface microstructure.

Dynamic mechanical thermal analysis (DMTA)

A TA Instruments DMA Q800 (TA Instruments Inc., Newcastle DE) was employed to determine the dynamic mechanical properties of the copolymers in tensile mode. Heating and cooling rates of 3 °C/min, and a sampling rate of 1 Hz, were used for all DMA tests.

Results and discussion

Cellulose nanowhiskers obtained from acid hydrolysis are needle-shaped. Figure 1 shows the morphology of cellulose nanowhiskers cast on glass slides. The dimensions of the cellulose nanowhiskers based on this atomic force microscope (AFM) image are 10 nm in diameter with an aspect ratio in the range of 30–100. These nanowhiskers will act as the reinforcement phase in all the cellulose nanocomposites. Cellulose nanowhiskers have the same chemical structure as that of the matrix pulp, which is also made of cellulose, and hence, the reinforcing phase and the pulp matrix are naturally compatible. The strong hydrogen bonds between the two components guarantee the efficient transfer of load from the matrix to the reinforcing nanowhiskers, while preventing the delamination that is common in fiber-reinforced composites.

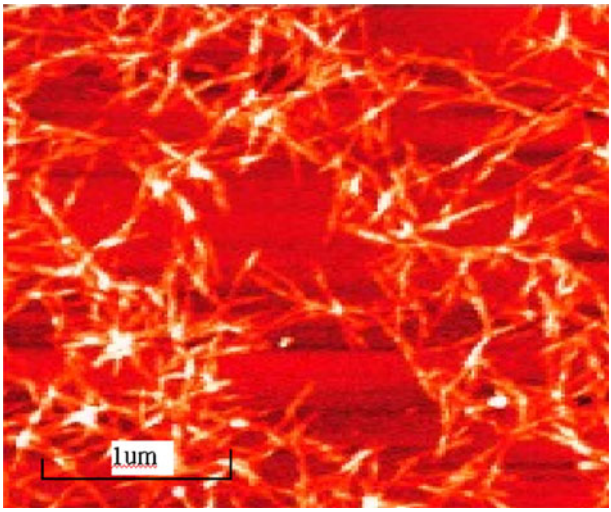

Fig. 1 AFM micrograph of cellulose nanowhiskers dried from an aqueous suspension on a glass slide

Figure 2 shows ESEM micrographs of the all-cellulose nanocomposites at different magnifications. The accelerating voltage is kept as low as 2 kV to avoid surface damage and charging. The microstructure of the all-cellulose nanocomposites fabricated in the absence of a magnetic field is shown in Fig. 2a, b. Large fibers from the pulp are clearly demonstrated at low magnification. The diameter of the pulp cellulose fiber is around 20 μm. Cellulose nanowhiskers are shown at higher magnification. Fabricated in the absence of an externally applied magnetic field, the cellulose nanowhiskers are randomly oriented. The microstructures of the all-cellulose nanocomposites fabricated under magnetic field are shown in Fig. 2c, d. Comparing with the nanocomposites created in the absence of a magnetic field, no difference at low magnification may be observed. It seems that the magnetic field has little impact on the morphology of the matrix, i.e., the large cellulose fibers. Conversely, the higher magnification reveals considerable morphological differences between the nanocomposites fabricated in the presence of a magnetic field as compared with those fabricated in the absence of a magnetic field. When subjected to a magnetic field, the slender nanowhisker fibers become aligned perpendicular to the magnetic field. This phenomenon is due to the anisotropic diamagnetic susceptibility of the cellulose nanowhiskers. The diamagnetic susceptibility of the nanowhiskers in the direction of the whisker axis is smaller than the direction perpendicular to the whisker axis. The helical axis aligns along the applied field. Because the helical axis is perpendicular to the whisker axis, the whiskers will align perpendicular to the magnetic field. This magnetic alignment phenomenon has been reported in nanowhisker suspensions [11–14] and nanocomposites composed of cellulose nanowhiskers and polyvinyl alcohol [15]. Our results show that the magnetic field will align the nanowhisker in the fabricated all-cellulose nanocomposite, while it will not have any influence on the orientation distribution of the cellulose pulp fibers. The difference in the response to the externally applied

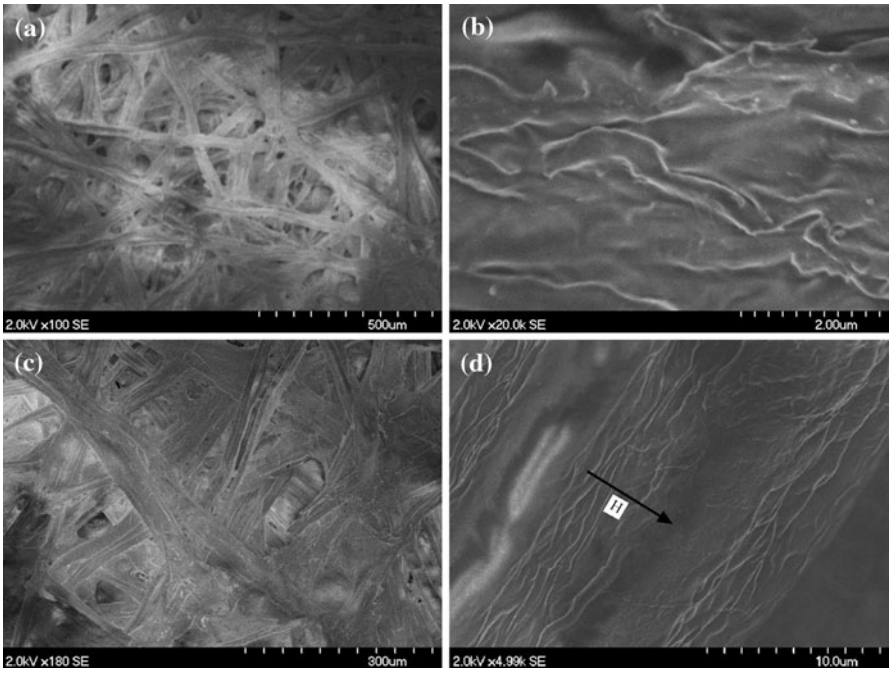

Fig. 2 ESEM micrographs of an all-cellulose nanocomposite fabricated as follows: **a** low magnification and **b** high magnification, both in the absence of a magnetic field; **c** low magnification and **d** high magnification, both subjected to an externally applied magnetic field

magnetic field between these two types of cellulose fibers is due primarily to their size effect. Large pulp fibers prevent free movement and limit the realignment of pulp fibers. The rotation force generated by the diamagnetic susceptibility is not large enough to rotate the pulp fibers, but it is sufficient to promote the rotation of the nanowhiskers when they are not strongly bounded to neighboring pulp fibers.

In the all-cellulose nanocomposites, the nanowhiskers act as the mechanical reinforcement phase. The storage moduli of a paper sheet without cellulose nanowhiskers and of an all-cellulose nanocomposite containing nanowhiskers are compared in Fig. 3. The presence of 5% (by weight) cellulose nanowhiskers in the composites increased the storage modulus almost by one order of magnitude, from 652 MPa for the paper sheet to 4884 MPa for the nanocomposite along the direction perpendicular to the applied magnetic field direction at 20 °C.

Figure 3 also illustrates the anisotropy of the storage modulus in the nanocomposites fabricated under a magnetic field, which is due to the alignment of the cellulose nanowhiskers. Cellulose nanowhiskers are aligned perpendicular to the magnetic field. As a result, the storage modulus along the direction perpendicular to the magnetic field is much higher than that parallel to the magnetic field. Storage modulus of cellulose nanowhiskers composite fabricated without magnetic field falls in the middle of the properties measured in the two directions of the anisotropic sample. At 20 °C, the storage modulus along the direction perpendicular to the

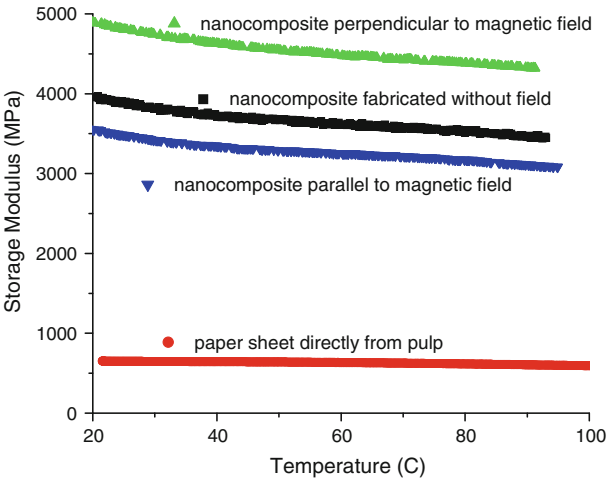

Fig. 3 The storage moduli of paper sheets from the fir pulp and of all-cellulose nanocomposites reinforced with cellulose nanowhiskers

magnetic field is 4884 MPa, while the storage modulus along the direction parallel to the magnetic field is 3568 MPa. For the isotropic sample fabricated without the magnetic field, the storage modulus is 3955 MPa. It is important to note, however, that even though the storage modulus along the direction parallel to the magnetic field is smaller than that measured perpendicular to the magnetic field, it is still considerably higher than the storage modulus measured for paper sheets without the nanowhiskers, thus highlighting the reinforcing effect of these cellulose nanofibers.

Conclusions

Cellulose nanowhiskers in all-cellulose nanocomposites act as reinforcement fibers, increasing the storage modulus from 652 MPa to 4.88 GPa. Fabrication under a magnetic field caused the alignment of the cellulose nanowhiskers in the nanocomposites, with little effect on the orientation of the cellulose pulp fibers. Aligned cellulose nanowhiskers introduced anisotropy in all-cellulose nanocomposites. The storage modulus along the direction perpendicular to the magnetic field is much stronger than that parallel to the magnetic field. Cellulose nanowhiskers in this new all-cellulose nanocomposite increases strength dramatically. A magnetic field aligned the nanowhiskers and introduced an interesting fabrication parameter to tailor microstructure. By substituting for oil-based plastics, this sustainable cellulose nanocomposite can also help our economy decrease the dependency on imported oil.

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