Magnetically Active Composite Cellulose Fibers

Marcin Rubacha

Man-Made Fibers Department, Technical University of Lodz, 90–543 Lodz, Poland

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ABSTRACT: A process has been developed for manufacturing magnetically active composite fibers of cellulose using *N*-methylmorpholine-*N*-oxide as a direct solvent for this natural polymer. Owing to its elasticity and stability, the process made it possible to add considerable quantities of modifier (up to 50% of fiber weight) to spinning solutions. The incorporation of powdered hard ferrites (barium ferrite) into the polymer solution resulted in fibers with magnetic properties, which exhibited a uniform distribution of the modifier. The results of testing the magnetic properties of the fibers obtained have shown that the coercive force of fibers do not depend on the modifier content, while the residual magnetism increases with the content of the ferromagnetic material. The value of fiber remanence is a fraction of the value of magnetic material remanence, corresponding to its volume content in fibers. This may indicate that the modifier used is chemically stable in the spinning solution medium. The thermal analysis of the fibers (DSC and TGA) has shown no negative effect of the modifiers on the fibers' thermal stability. An undesirable influence of the ferromagnetic compound on the fibers is the deterioration of their mechanical properties. © 2006 Wiley Periodicals, Inc. J Appl Polym Sci 101: 1529–1534, 2006

Key words: composites; fibers; magnetic polymers

INTRODUCTION

The advance of civilization and the related phenomenon of human investigation of new fields of activities, as well as the permanent aspiration to improve the comfort of life, are all incentives to search for new and better materials. Materials with new, specific properties that are characterized by low manufacturing costs can be found among the composites. The present study presents a process for manufacturing composite cellulose fibers that interact with a magnetic field. The fibers were spun by the method using *N*-methylmorpholine-*N*-oxide hydrate (NMMO) as a direct solvent for cellulose. This technology is an interesting alternative to conventional methods of manufacturing cellulose fibers, as it is free from the serious drawbacks of the latter. In addition, the NMMO process is characterized by a short and simple production cycle, which is also environmental friendly because of its closed solvent circulation. Another characteristic feature of this process is its elasticity and the ease of producing concentrated and homogeneous solutions of cellulose.[1,2]

The above-mentioned features of this process allow far-reaching changes to be made in:

- the composition of the solution,
- the conditions of cellulose dissolution,
- the conditions of fiber spinning.

These properties allowed us to use a fiber modification technique by incorporating a powdered modifier into the cellulose solution. This technique is one of the most effective methods of imparting new features to fibers, as it guarantees their stability. By incorporating proper compounds into the fiber-forming polymer, one can, among other things, obtain improved electrical conductivity,[3,4] flame resistance,[5] UV shielding, and sensory properties.[6]

EXPERIMENTAL

The fibers under investigation were spun from cellulose solutions in NMMO hydrate by the dry–wet process. To prepare spinning solutions, Russian cellulose KCBK with alpha cellulose content 94.1% and degree of polymerization equal to 795.

Cellulose dissolving was carried out in IKA VISC MKD 0.6-H60 reactor equipped with heating jacket and stirrers. The effect of this process was 12% homogenous cellulose solution in NMMO. From the obtained solutions, fibers were formed and solidified in aqueous coagulation bath prior to being put into plasticization aqueous bath. Fibers obtained in this way were rinsed in water and dried. The scheme of cellulose dissolution process and fiber spinning is shown in Figure 1.

Correspondence to: M. Rubacha (mrubacha@mail.p.lodz.pl).
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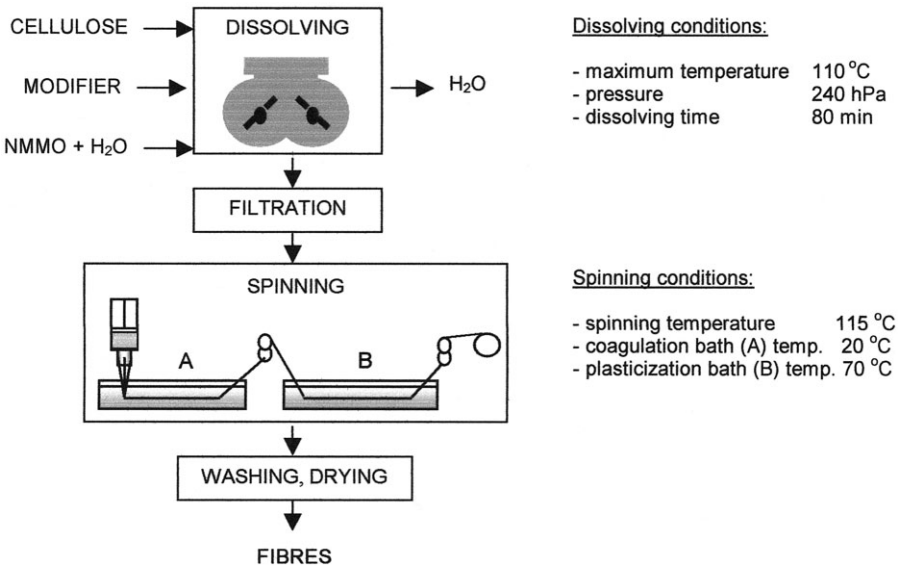

Figure 1 Scheme and conditions of the preparation of cellulose fibers modified with a magnetic powder.

The performed investigations and tests confirmed the possibilities of filling cellulose fibers with magnetically active powders. The results obtained also indicate possible fields of application for such fibers, including for protective clothing against magnetic fields, separators, filters, etc.

Hard barium ferrite with a composition of $BaFe_{12}O_{19}$ was produced in ZM Trzebinia factory in Trzebinia, Poland. Before being used for the modification of cellulose fibers, modifier was subjected to a complete process of ferrite-forming process and grinding. This magnetic powder was characterized by a considerable particle size amounting to 9 μm, and a particle size distribution as shown in Figure 2.

The ferromagnetic compound was added to the spinning solution in such quantities that could provide its content in final fibers from 10 to 50 wt %. Fibers were spun with two spinning rates: V_1 = 35 m/min and V_2 = 70 m/min. At the solution feeding rate V_o = 1, these spinning conditions allowed us to obtain 35- and 70-fold draw ratios, respectively.

The resultant fibers were tested to assess the magnetic effect obtained, and their suitability for textile processing. The magnetic properties were tested by means of a vibratory magnetometer LakeShore VSM 7307. Fiber tenacity was measured with a materials testing machine Zwick Z 2.5/TN18. Testing the tenacity of fibers was based on constant speed elongation of elementary fiber with simultaneous strength measurement. The device allowed to establish such parameters as tenacity, initial modulus, and elongation at break. Sorption properties were assessed by standard methods. Thermal analysis of fibers was carried out by the thermogravimetric analysis (TGA) and DSC methods. Measurements were done with the use of Perkin–Elmer TGA6 and DSC6 devices. Density of fibers was established with the use of pycnometer method.

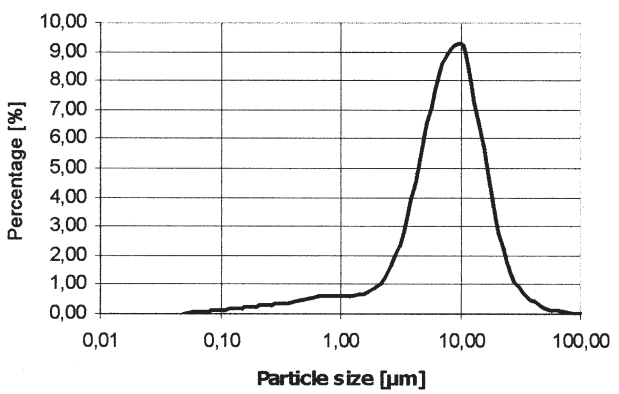

Figure 2 Hard ferrite particle size distribution.

RESULTS AND DISCUSSION

The powdered ferromagnetic material was added to the mixture of cellulose, solvent, and stabilizer at the beginning of cellulose dissolution during intensive stirring, which made it possible to uniformly distribute the modifier in the solution. Good component intermixing allowed us to form fibers with a uniformly distributed magnetic phase within their entire volume (Fig. 3).

The TGA of the obtained fibers has shown that the actual content of modifier was different from the expected value (Table I). The differences of several percents between the desired and actual modifier content in fibers are due to the deposition of greater ferromagnetic particles on the filter of the spinning machine. In

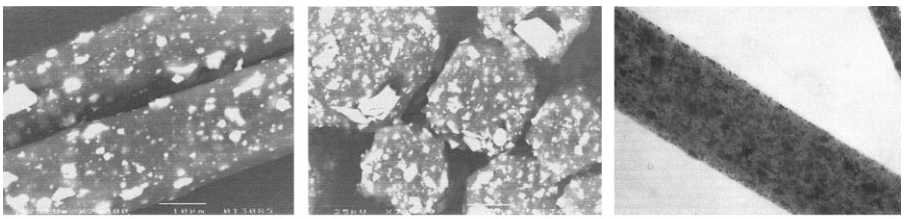

Figure 3 Microstructure of cellulose fibers containing 19 wt % of magnetic modifier: (a) and (b) SEM images; (c) optical microscope image under transmitting light.

fact, the magnetic powder contents in fibers range from 3.1 to 23% of fiber volume.

The incorporation of ferromagnetic powder into the diamagnetic fibers resulted in a composite with new magnetic properties. The hysteresis loops of the composite fibers obtained are shown in Figure 4.

As expected, the remanence of fibers increases with the barium ferrite content in fibers. Its value is a fraction of the remanence value of the magnetic compound corresponding to its percentage content in fiber by volume. The coercive force value of fibers is approximately equal to that of the magnetic powder used (Fig. 5).

Any further increase in the value of remanence is possible only by incorporating more magnetic material into the fiber, but this possibility is limited, since higher quantities of the powdered modifier considerably deteriorate the processing capabilities of the spin-

TABLE I
Composition of Fibers Modified with Magnetic Powder

Fiber number	Desired content of magnetic modifier (wt %)	Actual content of magnetic modifier (wt %)	Actual content of magnetic modifier (wt %)	Fiber density (g/cm^3)
1	Unmodified fibers	—	—	1.53
2	10	9.5	3.1	1.60
3	15	14.5	5.4	1.71
4	20	19.0	7.1	1.75
5	25	24.0	9.3	1.87
6	30	28.5	11.2	1.90
7	40	38.0	16.6	2.09
8	50	48.0	23.0	2.29

Density of barium ferrite is 4.72 g/cm^3.

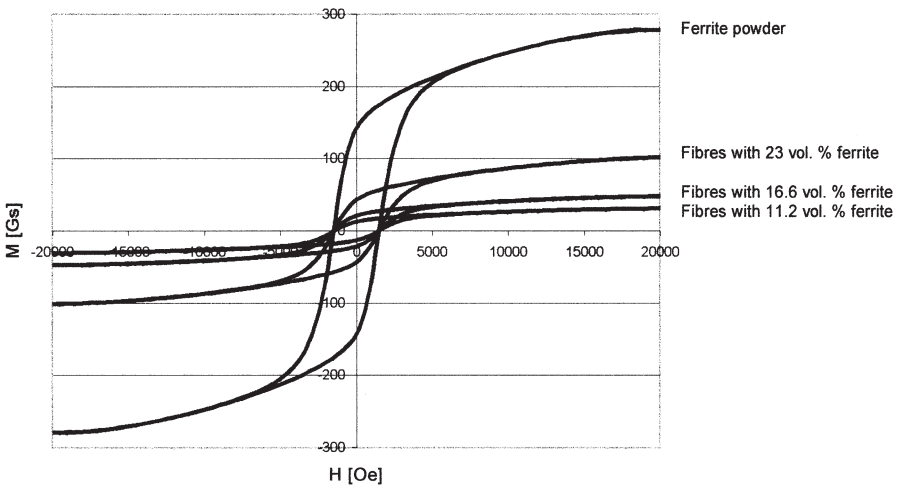

Figure 4 Selected hysteresis loops for composite fibers containing 11.2, 16.6, and 23.0 vol % of hard ferrite powder.

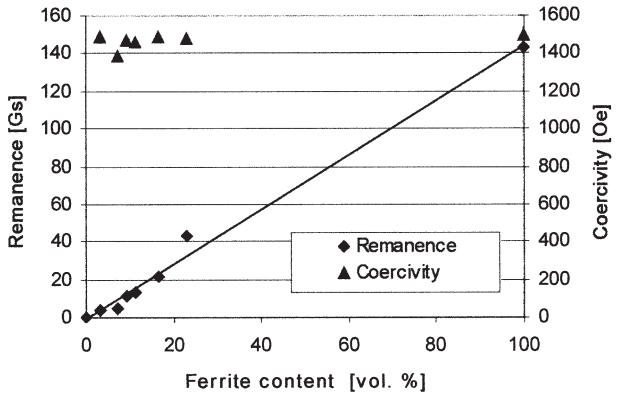

Figure 5 Effect of hard ferrite on the coercive force and remanence of fibers.

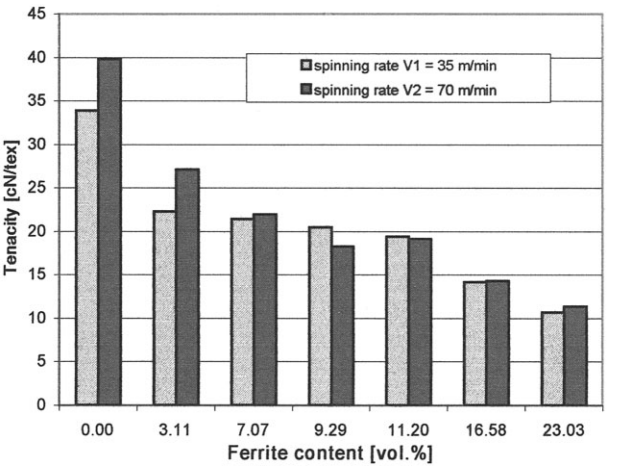

Figure 7 Dependence of fiber tenacity on ferrite content and spinning rates.

ning solution. Presumably, a solution to this problem might be the use of ferromagnetic powders with a smaller particles diameter ($d < 3$ μm) and a lower size spread. The use of powders that met these requirements would prevent disturbances during fiber formation and magnetic material deposition on the spinning machine filter. Magnetic powders with higher particle size reduction may also result in better magnetic properties of ferromagnetic material. This concerns hard magnetic compounds that are characterized by a high coercive force value. Particles of such ferromagnetic materials act as single magnets, so it would be best to use powders with nanometric particle sizes.[5]

As expected, the presence of modifier particles in fibers value affects also their other properties. It has been found that the strength properties of the modified fibers depend to a large extent on the magnetic modifier content. The diameters of fibers formed with a spinning rate of 35 m/min ranged from 23.5 to 26 μm, while the fibers formed at twice as high a spinning rate were considerably thinner, their diameters ranging from 15.1 to 18.8 μm. The increase in the magnetic compound content resulted in an increased linear density of fibers and deteriorated tenacity and initial modulus (Figs. 6, 7, and 8).

It was also found that most of the physical and mechanical properties of fibers are strongly affected by the draw ratio used. The increase in the modifier content in fibers formed at the lower rate causes no greater differences in fiber elongation at break. This dependence changes for fibers spun at twice as high a rate, where a considerable reduction in elongation is observed (Fig. 9). A significant effect of the draw ratio on fiber tenacity was observed only in the case of fibers with a low modifier content, while the tenacity of fibers with higher magnetic material contents does not depend on the draw ratio (Fig. 7). The reduction in the strength of magnetic powder-containing fibers is

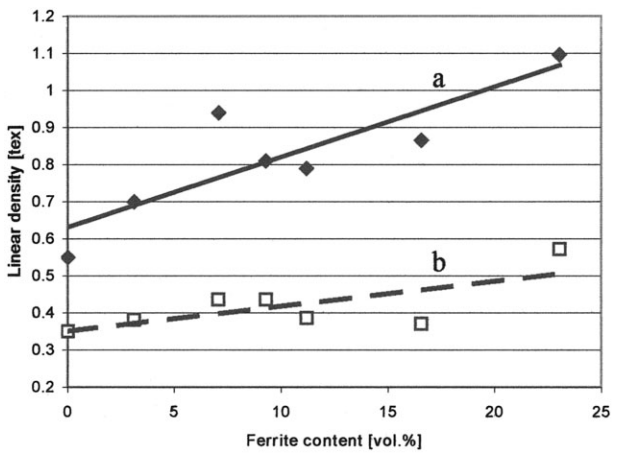

Figure 6 Dependence of fiber linear density of ferrite content: (a) fibers spun at V_1 = 35 m/min; (b) fibers spun at V_2 = 70 m/min.

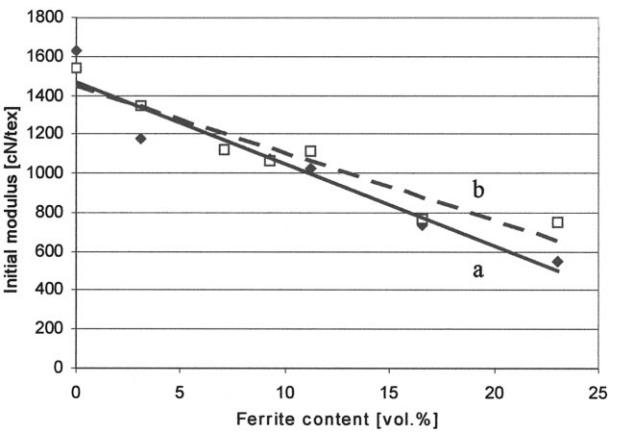

Figure 8 Dependence of fiber initial modulus on ferrite content: (a) fibers spun at V_1 = 35 m/min; (b) fibers spun at V_2 = 70 m/min.

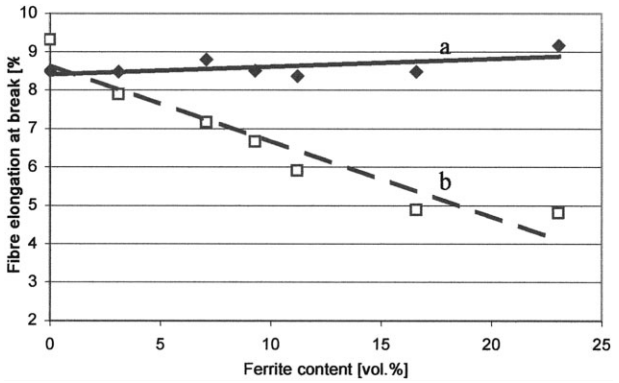

Figure 9 Dependence of fiber elongation at break on ferrite content: (a) fibers spun at $V_1 = 35$ m/min; (b) fibers spun at $V_2 = 70$ m/min.

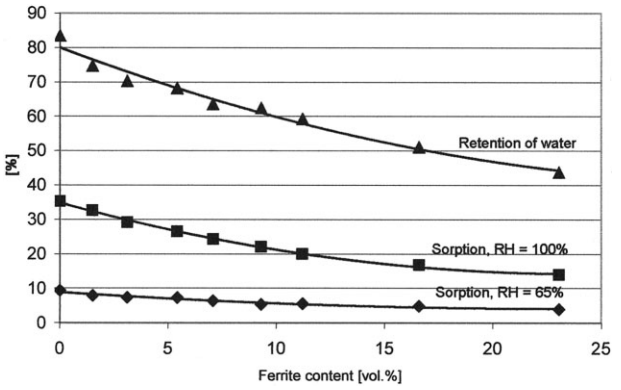

Figure 11 Sorption properties of fibers with various barium ferrite contents.

due, among other things, to considerable differences in the properties of composite components. In this case, the fiber deformation leads to the formation of structure discontinuity at the border between the cellulose matrix and modifier particles.[7]

The results of thermal analysis have shown that the modifier content exerts no practical influence on the thermal stability of fibers. DSC and TGA measurements show only an inconsiderable decrease in the temperature of cellulose thermal decomposition. On the other hand, it has been observed that with the increase in modifier content in fibers subject to a complete decomposition of the cellulose matrix, a constant weight of the residue is obtained at lower and lower temperatures (Fig. 10). The weights of residues of cellulose fibers subjected to thermal decomposition correspond approximately to the quantities of modifier incorporated into fibers.

On the basis of the TGA results, one may assume that the ferromagnetic material is resistant to the conditions of cellulose dissolution and the medium of the spinning solution. The chemical stability of the magnetic modifier is also confirmed by the fact that its presence in spinning solutions causes no changes in the polymerization degree of the cellulose matrix of final fibers.

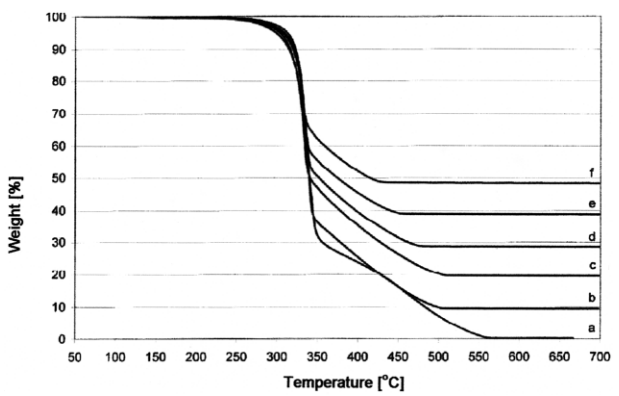

Figure 10 Diagram of TGA results of fibers modified with magnetic powder. Curve (a): unmodified fiber; curves (b–f): fibers containing 3.1, 7.1, 11.2, 16.6, and 23.0 vol % of barium ferrite.

Cellulose fibers are characterized by good sorption properties, which make them most suitable for clothing applications. However, the incorporation of a hydrophobic modifier causes considerable deterioration in both moisture absorption and retention of the modified fibers (Fig. 11).

One may assume that single particles of the modifier are too large to be capable of significantly developing both the external and internal surfaces of the fibers. The presence of the powdered magnetic compound does not cause any increase in the number of large pores in fibers, which could increase the retention value.

CONCLUSIONS

On the basis of the results obtained from the experiments and tests, it can be stated that the NMMO process makes it possible to prepare fibers with a permanent magnetic effect, which are suitable for further textile processing. The present study indicates how the method used can be modified to further improve the properties of modified fibers. There is still a real chance of improving both the magnetic effect and mechanical properties of the composite fibers. Further experiments with the use of powdered magnetic modifier should take into account the conclusions resulting from the studies performed, namely the necessity of using a modifier with considerably smaller particle size, and the optimization of the fiber-spinning process.

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