

Cellulose Fibers Modified by Silicon Dioxide Nanoparticles

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ABSTRACT: The sol-gel method is one of the most suitable ways for producing glasses, glass films, glass fibers, and glass nanoparticles. The relatively mild reaction conditions and simplicity of the sol-gel method make it an excellent tool for producing substances with precisely tailored properties. This technique opens the possibility for the synthesis of various new compounds, including pH sensors, ion sensors, bioactive nanoparticles, dyes carriers, and so forth. An attempt was made to combine the sol-gel technique with the advanced technology in the production of cellulose fibers in order to obtain fibers with new and unique properties. Cel-

lulose fibers were prepared with *N*-methylmorpholine-*N*-oxide as the direct solvent. The obtained fibers contained up to 30% (w/w) silicon dioxide nanoparticles. In order to observe the influence of the modifier on the fibers, their mechanical properties were examined. Modified fibers were also examined by means of thermogravimetry, wide-angle X-ray scattering, and ^{29}Si -NMR solid-state spectroscopy. © 2005 Wiley Periodicals, Inc. *J Appl Polym Sci* 98: 1793–1798, 2005

Key words: fibers; modification; polysaccharides; nanoparticles; silicas

INTRODUCTION

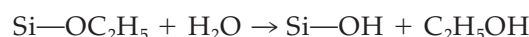
Cellulose is one of the natural polymers that have wide application in fiber production. However, cellulose fibers are obtained by several different methods. One of the newest and most advanced ways of producing cellulose fibers is the technology based on *N*-methylmorpholine-*N*-oxide (NMMO) as the cellulose solvent.^{1,2} NMMO technology is effective, relatively simple, and environmentally friendly. Because the parameters of the process can be easily changed over a wide range, the method produces fibers with precisely designed properties. The simplicity and flexibility of the process make it possible to introduce various types of modifiers at almost any stage of the process. Cellulose fibers obtained by this technology have very good functional quality, which makes them excellent materials for the production of clothing.

In the present research we attempted to produce modified cellulose fibers with nanoparticles of silicon dioxide. The nanoparticles, having a typical diameter of <100 nm, are very promising as modifiers of polymeric materials^{3–5} because of their unique structure and special surface properties. The amorphous silicon dioxide nanoparticles are chemically stable and non-toxic, and the synthesis methods by sol-gel techniques are relatively simple. Moreover, use of the

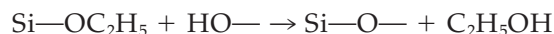
sol-gel method makes it possible to obtain well-defined products with uniform particle size,^{6,7} which is very important from the fiber industry point of view. Another advantage of the sol-gel method is that the silicon dioxide particles can be doped^{8,9} or chemically modified¹⁰ with a wide range of active compounds.

In the sol-gel process for preparation of glass particles, tetraethoxysilane is usually used as a precursor.^{11,12} Hydrolysis and condensation reactions take place during the process as follows:

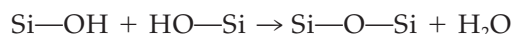
(i) hydrolysis:



(ii) alcohol condensation:



(iii) and water condensation¹³:



Depending on the reaction conditions (pH of the starting solution, precursor type, nature of the catalyst, ratio of the starting materials), different types of glass materials can be obtained.⁷

When the precursor is an $\text{Si}(\text{OR})_4$ type compound, the product of the polycondensation reactions is a typical inorganic glass type material having only OH groups on the surface. The organically modified silane (ormosil) type of material can be synthesized from precursor types $\text{R}'\text{Si}(\text{OR})_3$ or $\text{R}'\text{R}''\text{Si}(\text{OR})_2$, where R'

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and R'' are the functional groups.¹⁴ Depending on the type of functional groups (R', R''), it is possible to obtain glasslike material with specific and well-defined properties. Such a material can be applied as a pH sensor, ion sensor, luminescent and thermochromic materials, bioactive compounds, and so forth.

This study attempted to obtain cellulose fibers modified with model silicon dioxide nanoparticles. The results of the research yielded information for the further synthesis of new interactive cellulose fibers modified by multifunctionalized ormosil-type nanoparticles.

EXPERIMENTAL

Materials

Colloidal silica particles (Ludox SM-30 type, GRACE Davison) were applied in the present research. A model silica was used that had 7 nm particles, a specific surface area of 320–400 m²/g, and a pH of 10.2.

Spruce cellulose (DP 810) was used for the preparation of cellulose fibers. A 50% water solution of NMMO was purchased from Hustman Co. The antioxidant propyl ester of gallic acid (Tenox PG) was purchased from Aldrich.

Instrumentation

The spinning dopes were made using a laboratory scale knitter (IKA-VISC), and a small spinning device was used for the preparation of cellulose fibers.

Thermogravimetric analysis (TGA) was performed using a Perkin–Elmer TGA-6 device. Measurements were carried out in the range of temperatures from 100 to 800°C.

²⁹Si-NMR solid-state spectra were acquired using a Bruker DSX-300 NMR spectrometer.

Wide-angle X-ray scattering (WAXS) was performed with a Siemens DV 5000 polycrystalline diffractometer.

The mechanical properties of cellulose fibers were checked on a Zwick Z2.5/TN1S tensile testing machine.

Preparation of cellulose fibers

The cellulose fibers were prepared by means of the NMMO method. The spinning dope was prepared as follows: spruce cellulose was mixed with a 50% water solution of NMMO, and then the antioxidant (1%, w/w, calcd for α -cellulose content) together with a colloidal silicon water dispersion of Ludox was added. The dispersion was added to the starting mixture of cellulose and 50% NMMO in an appropriate quantity to reach a suitable concentration between 0.5 and 30% (w/w) of silicon dioxide in the dry cellulose fibers.

The mixture of cellulose, NMMO, and modifier was vigorously stirred and heated, and excess water was removed under low-pressure conditions. The process was continued until the appropriate quantity of water was collected and a homogenous and transparent solution of cellulose was obtained.

The cellulose fibers were obtained by means of the dry–wet spinning method as follows: the cellulose solution in NMMO was placed into the spinning device and then pressed out by a piston moving with constant velocity. The spinning solution was spun from an 18-hole spinneret. The cellulose fibers were solidified in a coagulation bath containing cold water. Then, they were washed in the hot water bath, dried, and examined.

RESULTS AND DISCUSSION

Determination of silicon dioxide content

To prove that the cellulose fibers contain silicon dioxide, the particles were examined by means of TGA. These analyses were carried out on the Perkin–Elmer TGA-6 in a temperature range between 100 and 800°C. In the first step of the measurement, 40–50 mg of powdered cellulose fibers were dried in the TG device oven in an atmosphere of dry gas at 105°C. The drying mode usually lasted 20 min until no further weight loss of the sample was observed. Then, the sample was again tarred and heated to 800°C at a rate of 10°C/min. Examples of the TGA of the cellulose fibers without additives and containing 9.09, 16.67, and 30.0% colloid Ludox SM-30 type silicon particles are shown in Figure 1.

According to the TGA, it is clear that the silicon dioxide nanoparticles introduced at the beginning of the dissolution process of the cellulose in NMMO still remain in the final fiber material. The calculated amounts of silicon dioxide nanoparticles in the fibers as determined by means of the TG method are shown in Table I.

Although there are differences between the theoretically calculated amounts of silicon dioxide in the fibers and the experimentally determined amounts, the correlation of the obtained data is very strong. In some cases the decrement of silicon dioxide particles in the cellulose fibers can be explained by the fact that, during the cellulose dissolution process with rising temperatures and in the presence of basic solvent, some silicon dioxide particles can be destroyed, dissolved, and finally removed together with the solvent during the fiber solidification process.

Nevertheless, even in the worst case that was observed, more than 83% of the modifier introduced in the beginning of the cellulose dissolution process still remained in the final cellulose fibers. The data collected by the TG method were proved by the analysis

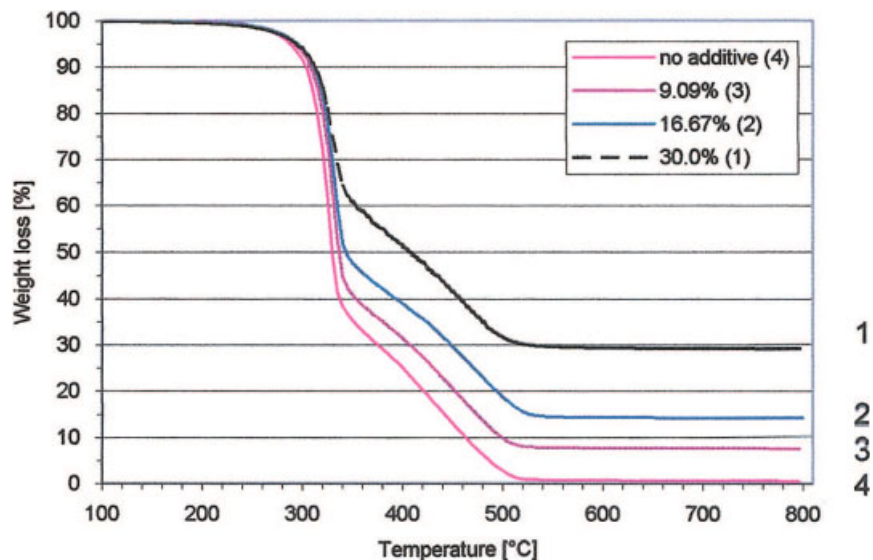


Figure 1 The thermogravimetric analysis for fibers containing colloidal silicon dioxide (LUDOX SM-30 type).

of ^{29}Si -NMR solid-state spectroscopy that was performed for cellulose fibers without any modifier addition and for fibers containing 16.67 and 30% silicon dioxide (Fig. 2). The spectra shown in Figure 2 are rather typical for the silicate phase with shifted signals at -99.6 and -109.4 ppm.

Unfortunately, because the concentration of silicon atoms was too low in the materials we examined, some difficulties were encountered in the measurements for fibers containing less than 16% silicon dioxide.

WAXS

In order to assess the changes in the crystallinity of the modified fibers, the fiber samples were examined by means of WAXS spectroscopy with 2θ angles between 0 and 50° . Roentgenograms of silicon dioxide modi-

fied fibers are shown in Figure 3. The estimation of the degree of crystallinity of the fibers was based on the calculation of the ratios of the surface areas corresponding to the crystal part of the sample and the total area of the spectrum. The changes in the degree of crystallinity corresponding to the silicon dioxide concentration in the fibers are shown in Figure 4.

The decreasing tendency of the degree of crystallinity of the cellulose fibers is obvious and can be simply explained by the rise in the concentration of silicon dioxide nanoparticles. Because silicon dioxide nanoparticles are amorphous, the higher concentration of the modifier will certainly cause a rise in the amorphous phase in the material of the fibers. Unfortunately, the analysis made by WAXS spectroscopy did not answer the question of how the silicon dioxide nanoparticles affect the crystallinity of cellulose during the spinning process.

TABLE I
Calculated Amounts of Concentration of Silicon Dioxide Particles in Cellulose Fibers as Determined by TG Method and Elemental Analysis

Calculated	Amounts of Silicon Dioxide (%)	
	TG method	Elemental analysis
0.00	0.46	0.31
0.50	0.66	0.85
0.99	1.00	1.20
2.44	3.56	3.22
4.76	5.11	4.68
6.98	7.51	7.79
9.09	7.88	9.14
16.67	14.03	13.88
30.00	29.07	28.39

Mechanical properties of cellulose fibers modified by silicon dioxide nanoparticles

The influence of the concentration of different silicon dioxide particles on the mechanical properties of the fibers was examined. The mechanical properties of the cellulose fibers were checked on the Zwick tensile testing machine. The tenacity and ultimate elongation of the cellulose fibers containing Ludox SM-30 type silicon dioxide particles are shown in Figures 5 and 6, respectively.

As expected, the tenacity of the cellulose fibers decreased when the concentration of silica particles rose. The addition of silicon dioxide particles up to 15% (w/w) caused a linear dependence in the drop of the fiber tenacity. Further increasing the silicon dioxide

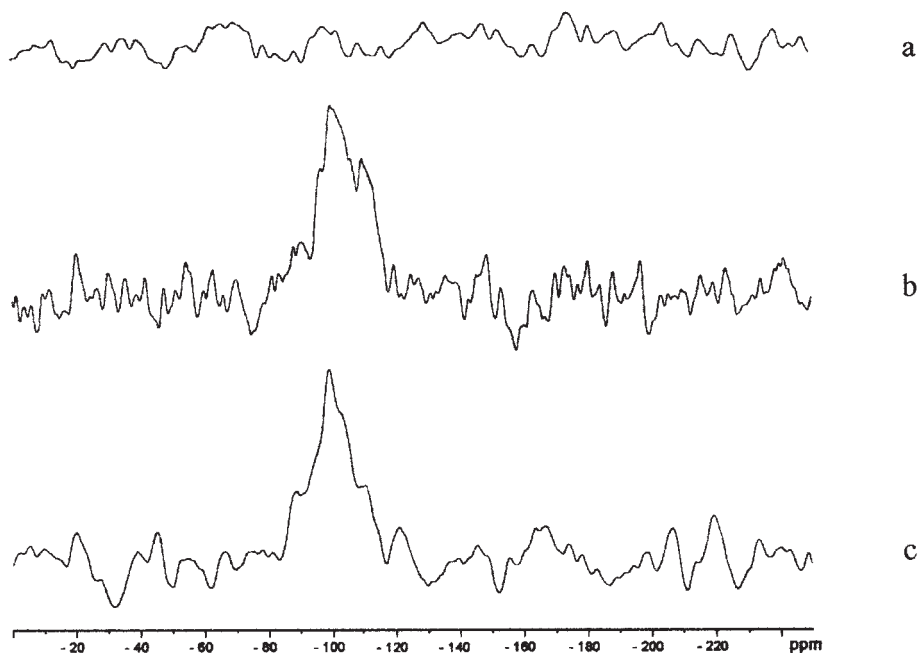


Figure 2 The ^{29}Si -NMR solid-state spectra for cellulose fibers without silicon modifier (spectrum a), with 16.67% silicon dioxide (spectrum b), or with 30.00% silicon dioxide (spectrum c).

particles in the cellulose fibers caused relatively small declines in the fiber tenacity. However, in the present phase of research in which up to 30% (w/w) silicon particles were added, we presume that in order to modify the cellulose fiber properties it would be sufficient to introduce only 7–10% (w/w) of the modifier. Such an amount of modifier would cause only about a 20% drop in tenacity of the modified fibers, which could be acceptable in some applications.

A nearly linear dependency was observed between the silicon dioxide nanoparticle concentration in the fibers and the elongation of the fibers. The addition of 30% (w/w) silicon dioxide nanoparticles caused about a 30% increase in the elongation of the cellulose fibers. The effect of the rise in elongation together with the rising concentration of silicon particles in the fibers can be explained by the plasticization effect of the silicon dioxide particles.

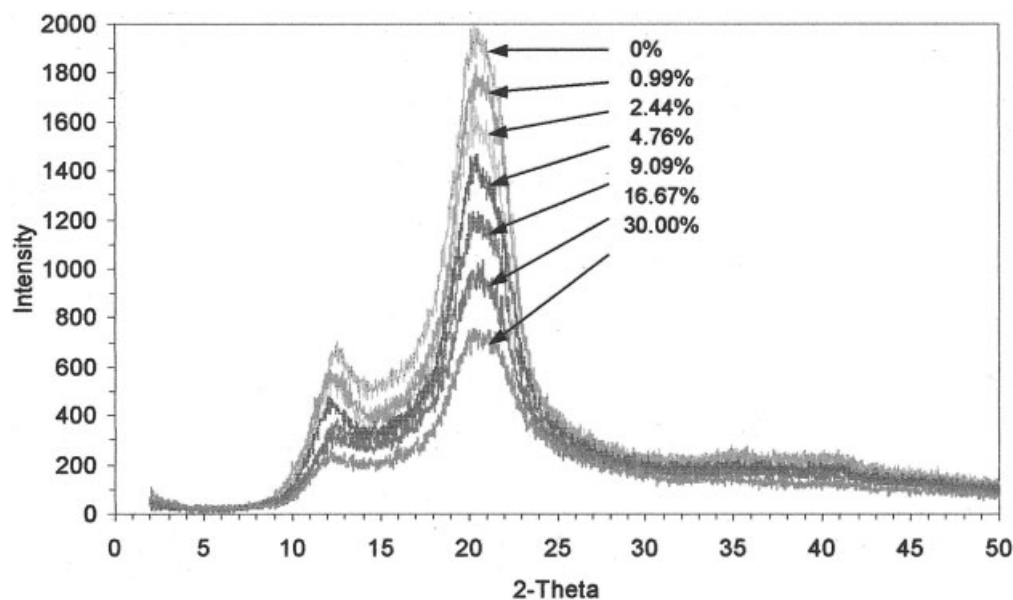


Figure 3 Wide-angle X-ray spectra for cellulose fibers containing silicon dioxide.

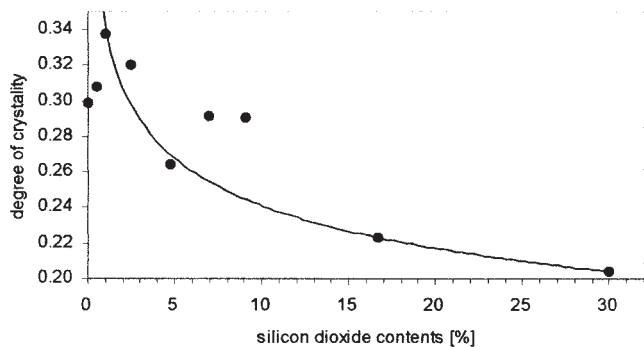


Figure 4 The degree of crystallinity of the cellulose fibers versus the concentration of silicon dioxide particles.

Estimation of average nanoparticle distribution

The average distribution of particles in the polymeric matrices can be described using three values, which are schematically shown in Figure 7. The a value concerns the size of the edge of an imaginary cube of a polymer that contains one spherical particle of modifier with a diameter of $2r$. The l value is the average distance between the two nearest particles of the modifier. To calculate the theoretical average distribution of silica dioxide nanoparticles in cellulose matrices, the density of the modifier and the density of the cellulose should be known. It is commonly known that the density of a material is additive and is the result of the density and contents of all components present in the material. Thus, the density of modified cellulose fibers will be the result of the density and contents of modifier and cellulose as well. Therefore, the density of cellulose fibers with different concentrations of silica dioxide nanoparticles was determined in density gradient columns containing a mixture of toluene and carbon tetrachloride. The estimation of the density for pure silicon dioxide nanoparticles was done using extrapolation. It was considered possible that silicon particles can affect the solidification and crystalliza-

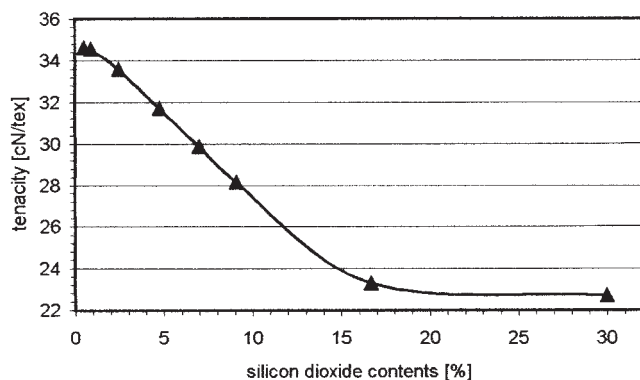


Figure 5 The tenacity of the cellulose fibers versus the concentration of silicon dioxide particles.

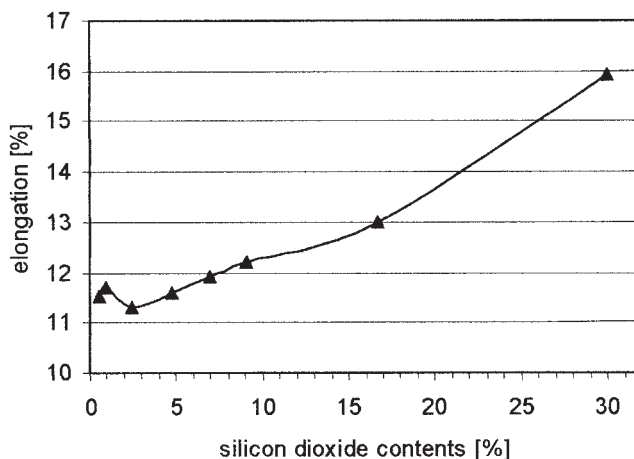


Figure 6 The elongation of the cellulose fibers versus the concentration of silicon dioxide particles.

tion of cellulose fibers during the spinning process, which means that the degree of crystallinity of fibers can finally affect the estimated density value of silicon particles. Because the influence of modifier on the fiber crystallinity is not clear, an additional measurement was carried out. In this method, a cellulose was used that was chemically and physically unchanged by the dissolution and spinning process. A certain amount of the water dispersion of silicon dioxide nanoparticles was spread onto dry and weighted spruce cellulose sheets. The sheets were redried, and the density of the samples of cellulose prepared in that manner was determined. The density values for the pure silicon dioxide nanoparticles were extrapolated. The density values for pure silicon dioxide nanoparticles determined by means of the two mentioned methods differed by about 0.6%. The diameters of the silicon di-

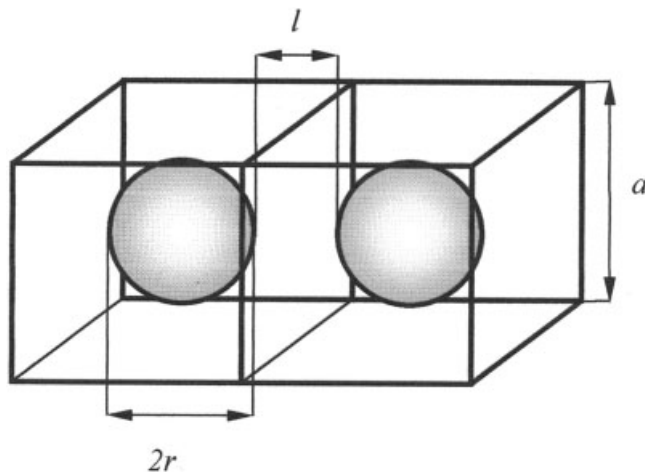


Figure 7 The modifier mean distribution in the polymeric matrices as described by three values: a , the edge size of the polymer cube; l , the average distance between particles of the modifier, and $2r$, the particle diameter.

TABLE II
Average Values of *a* and *l* for Cellulose Fibers
Containing Different Concentrations of Silicon Dioxide
Nanoparticles

Theor silicon dioxide contents in cellulose fibers (%)	<i>a</i> (nm)	<i>l</i> (nm)
0.5	35.6	28.6
0.99	28.3	21.3
2.44	21.0	14.0
4.76	16.8	9.8
6.98	14.7	7.7
9.09	13.5	6.5
16.67	10.9	3.9
30.00	8.9	1.9

oxide nanoparticles were based on the data sheet provided by GRACE Davison.¹⁵

CONCLUSIONS

Cellulose fibers modified with Ludox SM-30 type silicon dioxide nanoparticles were prepared. The concentration of nanoparticles in the cellulose fibers varied from 0.5 to 30% (w/w). The NMMO process proved to be quite suitable for the preparation of cellulose fibers modified with silicon dioxide particles. It was possible to introduce even 30% silicon modifiers into the cellulose fibers. TGA, elemental analysis, and solid-state ²⁹Si-NMR spectroscopy analysis showed that almost the entire amount of the silicon dioxide nanoparticles introduced in the beginning of the cellulose dissolution process remain in the cellulose fibers. Silicon dioxide particles in the cellulose fibers caused a decrease in the tenacity of the fibers and an increase in their elongation. Fibers containing 30% silicon dioxide nanoparticles had only about 30% lower tenacity than cellulose fibers without the modifier. It is well known that cellulose fibers obtained by the NMMO method have a tendency toward fibrilla-

tion.^{16,17} Our previous research results (data not shown) demonstrated that the presence of silicon dioxide nanoparticles in the fiber materials brings about a decrease in the fibrillation tendency.¹⁸

The sol-gel method makes it possible to synthesize silicon dioxide nanoparticles having various specific properties, such as pH sensing, ion sensing, bioactivity, luminescence, and so forth.

According to our results, we presume that it is possible to prepare interactive cellulose fibers modified with special silicon dioxide nanoparticles.

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