Cellulose Fibers Modified by Hydrophobic-Type Polymer

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ABSTRACT: In the present research, we discuss the influence of a hydrophobic modifier on the properties of cellulose fibers. The commercially available fluorocarbon polymer water dispersion was introduced in different concentration ratios to the spinning dope to change the physical properties of cellulose fibers. Cellulose fibers from *N*-methylmorpholine-*N*-oxide were prepared as a direct solvent. The fibers obtained contained up to 15% w/w of fluorocarbon polymer. To observe how the modifier influences the fibers' mechanical and thermal properties, fibrillation tendency and moisture absorption were examined. © 2007 Wiley Periodicals, Inc. J Appl Polym Sci 104: 398–409, 2007

Key words: fibers; modification; polysaccharides

INTRODUCTION

Cellulose is the natural and readily extractable source of raw material for the textile industry. However, while cellulose is disposed of in nature, it is unfortunately not soluble in common organic solvents, which is the main reason why the producing of cellulose fibers is so complex from the technological point of view. At present, several efficient cellulose solvent systems are known,[1–9] but only *N*-methylmorpholine-*N*-oxide (NMMO) seems the most promising cellulose solvent already used in the production of cellulose fibers.[10]

The main reason to modify the fibers is to change and improve the properties of the fibers obtained. The modification process improves their mechanical and chemical features, and gives them specific properties. Fibers with new properties make the final product more attractive, allowing the choice of goods to be widened. The production of man-made fibers can serve as a good example of how modification can change the final products. For man-made fibers, the modification can usually be carried out at any stage of fibers production, starting from the preparation of the spinning dope during the spinning process, processing the fibers, and up until the finishing process.

The relatively mild conditions for cellulose dissolution in NMMO allows a wide range of inorganic as well as organic modifiers to be introduced directly into the spinning dope. The properties of the cellulose fibers can be changed by the addition of substances, which are ideally insoluble in water and well dispersed, such as silicon dioxide particles,[11] carbon black,[12] particles with magnetic properties,[13] titanium dioxide particles,[14] materials with antibacterial properties,[15] and many others. The NMMO process is also suitable for modifications carried out with organic compounds of low molecular weight, as well as by polymers. The cellulose fibers can be successfully spun with the addition of such polymers as poly(ethylene oxide), which influences the porosity of the cellulose fibers,[16] polyethylene,[16] poly(vinyl acetate),[17] poly(vinyl alcohol),[18] and other polymers and copolymers.[19]

For cellulose fibers, modification of the grafted polymers can also be employed. Recent research shows that the addition of hydrolyzed starch-grafted polyacrylonitrile (HSPAN) superabsorbent to the cellulose solution in NMMO caused the water-absorbency to increase to 325 g/g (water/fiber).[20]

It is known that the Lyocell type has a rather high tendency to fibrillation.[21,22] This feature is undesirable in some situations and can be reduced by the addition of poly(vinyl alcohol) grafted onto the cellulose.[23]

The aim of the present study was to check the possibility of preparing the cellulose fibers modified by commercially-available hydrophobic water dispersion of fluorocarbon polymer. This product is usually used to finish the water-proof coating for cellulose fibers, but may also have potential application as a hydrophobic modifier of cellulose fibers.

EXPERIMENTAL

Materials

To prepare the cellulose fibers, cellulose with a polymerization degree (DP) of about 810 was used.

A 50% water solution of NMMO was purchased from Hustman (Hustman Holland BV) (Rotterdam, The Netherlands). The antioxidant propyl ester of gal-

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lic acid (Tenox® PG) was purchased from Aldrich Chemical (Gillingham, Dorset, UK).

As the cellulose fibers' modifier, we used the water dispersion Sevophob FTC, containing about 20% w/w of fluorocarbon resin from Textilcolor AG (Sevelen, Switzerland).

Instrumentation

The spinning dopes were made using a laboratory-scale knitter IKA-VISC Measuring Kneader MKD 0.6-H60 from IKA-Analysentechnik, (Heitersheim, Germany) and a small spinning device was used for the preparation of the cellulose fibers.

The differential scanning calorimetry (DSC) analysis was carried out with a Perkin–Elmer DSC-6 (US Instrument Division, Norwalk, CT) device. Measurements were carried out in the temperature range from 40 to 400°C.

The thermogravimetric (TG) analysis was carried out with a Perkin–Elmer TGA-6 (US Instrument Division, Norwalk, CT) device. Measurements were carried out in the temperature range from 100 to 800°C.

The mechanical properties of the cellulose fibers were checked on a Zwick Z2.5/TN1S tensile testing machine (Ulm, Germany).

A JEOL 5200 LV scanning electron microscope (SEM) (Tokyo, Japan) was used to examine the structure of the fibers obtained.

An optical Biolar microscope (Warsaw, Poland) coupled to a computer image analyzer was used to examine the degree of fibrillation of the modified cellulose fibers. The data was analyzed using Screen Measurement 32G/Mutech software.

Preparation of the 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, then the antioxidant (1% w/w, calculated for a-cellulose content) together with the Sevophob FTC water dispersion was added. The dispersion was added to the starting mixture of cellulose and 50% of NMMO in such a quantity, so as to reach a suitable concentration between 1.0 and 15% w/w of polymer in the dry cellulose fibers. The mixture of the cellulose, NMMO, and modifier was vigorously stirred and heated, and the excess water was removed under low-pressure conditions. The process was continued until the appropriate quantity of water was collected and a homogenous 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 at 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 washed in a hot water bath, dried, and examined.

FIBER EXAMINATION AND RESULTS

The fluorocarbon modifier content determination

Elemental analysis was used to estimate how much fluorocarbon modifier remained in the fibers obtained. The analysis was made for the plain fluorocarbon modifier, cellulose fibers without modifier, and for fibers containing the modifier. For all the above-mentioned samples, the elemental analysis for carbon, hydrogen, and fluorine content were carried out. The fiber samples were dried in 105°C for 30 min, then placed in an air-tight vessel. The preparation of the fluorocarbon polymer sample for elemental analysis was carried out in the following way: about 20 mL of the water dispersion of the fluorocarbon polymer was placed in a round flask heated to around 70°C, and the excess liquid was removed under low-pressure conditions. The waxlike remainder was heated for about 24 h at 120°C under low-pressure conditions to remove all volatile components. The results of the elemental analysis are shown in Table I.

For visualization purposes, the data presented in Table I was plotted as graphs. Thus, Figure 1 shows the dependence of carbon contents in the samples on the fluorocarbon modifier in the fibers. Figure 2 shows the dependence of fluorine contents in the samples on the modifier concentration in the fibers.

It is commonly known that there is a linear dependence between the elements contents in the sample and the composition of the samples. Thus, in Figures 1 and 2, the value ''0'' on the X axis refers correspondingly to the carbon and fluorine content for fibers without modifier (0% of modifier concentration). The ''100'' value on the X axis refers to the carbon or fluorine contents in the modifier only (100% of modifier concentration). All points between the ''0'' and ''100'' values refer to the fibers containing the fluorocarbon modifier.

The data obtained by elemental analysis shown in Figures 1 and 2 show a high linear dependence, with a mean square deviation R^2 coefficient equal to 0.9997 for the carbon data (Fig. 1) and with an R^2 coefficient equal to 0.9966 for fluorine (Fig. 2). However, in Table I, the data referring to the hydrogen contents in the samples are also shown, but the results are scattered and show no strong dependence. The results of elemental analysis carried out for the polymer modifier for fluorine content (shown in Table I) were not reliable. The results obtained proved to be lower by about half than those expected. Because the above

TABLE I
Content of Carbon, Hydrogen, and Fluorine in Modifier and in the Cellulose Fibers, as Determined by Elemental Analysis

Sample	Average carbon content (%)	Average hydrogen content (%)	Average fluorine content (%)
Cellulose fibers without modifier	40.60	6.33	0.083
Cellulose fibers with 1% of modifier	40.69	6.38	0.28
Cellulose fibers with 3% of modifier	40.87	6.32	0.49
Cellulose fibers with 5% of modifier	41.07	6.49	0.72
Cellulose fibers with 10% of modifier	41.56	6.43	1.26
Cellulose fibers with 15% of modifier	42.27	6.60	1.96
Modifier (dry substance)	52.32	7.14	6.95

results are not reliable, they were ultimately omitted from any further discussion.

Based on the elemental analysis results shown in Table I and Figures 1 and 2, the calculation of the real value of fluorocarbon polymer in each sample was made. The results are shown in Table II.

According to the elemental analysis results, it is clear that the fluorocarbon polymer introduced at the beginning of the dissolution process of the cellulose in NMMO still remains in the final fiber material. The calculated results based on the carbon content elemental analysis correspond quite well with the theoretically calculated values of the modifier concentration in the cellulose fibers. It appears that at least 75% of introduced polymer modifier remains in the fiber material.

Mechanical properties of cellulose fibers modified by fluorocarbon polymer

The influence of the concentration of different fluorocarbon polymer on the mechanical properties of the fibers was examined. The mechanical properties of cellulose fibers were checked on a Zwick tensile testing machine. T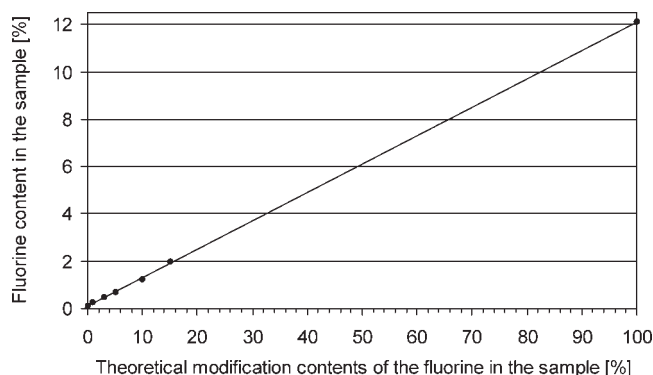he tenacity and ultimate elongation of the cellulose fibers containing fluorocarbon polymer are shown in Figures 3 and 4.

As expected, the tenacity of the cellulose fibers modified by fluorocarbon polymer decreased when the concentration of modifier rose. The addition of 15% (w/w) of fluorocarbon polymer caused a drop in fiber tenacity by about 30%, which is a relatively high value. The tenacity value drop of cellulose fibers containing fluorocarbon modifier is caused by the fact that the added polymer is not a spinnable material. It is rather obvious that the addition of nonfibrous polymer will cause the mechanical weakening of the fiber. More interesting is the fact that the addition of about 5% (w/w) of modifying polymer caused an increase of about 10% in the fibers' tenacity. It was observed that the spinning dope that contained the optimum concentration of modifying polymer had better spinnability. Good spinnability positively affects the mechanical properties of the fibers. The fluorocarbon polymer probably has a lubricating ability, which is most readily expressed within a certain concentration range.

This same characteristic local maximum can be observed in the relation between the concentration of modifier and the elongation (Fig. 4). The maximum elongation value occurs within a modifying polymer concentration range of about 5% (w/w). This may

Figure 1 Elemental analysis estimation of carbon content in the samples versus theoretically calculated modifier content.

Figure 2 Elemental analysis estimation of fluorine content in the samples versus theoretically calculated modifier content.

TABLE II
Concentrations of Fluorocarbon Polymer in the Cellulose Fibers

Sample	Theoretical concentration of the modifier (%)	Concentration of the modifier calculated on the basis of carbon contents (%)	Concentration of the modifier calculated on the basis of fluorine contents (%)
Cellulose fibers with 1% of modifier	1.00	0.77	2.1
Cellulose fibers with 3% of modifier	3.00	2.30	3.67
Cellulose fibers with 5% of modifier	5.00	3.93	5.39
Cellulose fibers with 10% of modifier	10.00	8.19	9.43
Cellulose fibers with 15% of modifier	15.00	14.25	14.67

suggest that even after fiber coagulation, the fluorocarbon polymer still has the lubricating ability, which helps the cellulose macromolecules to slip during the fibers' axial tension.

Thermal analysis

Thermogravimetric analysis

The influence of the modifier on the heat resistivity of the cellulose fibers was examined by means of thermogravimetric analysis with a Perkin–Elmer TGA-6 device. In the first stage of measurement, 40–50 mg of powdered cellulose fibers were dried in the thermogravimetric device oven in an atmosphere of dry gas at 105°C. The drying mode usually lasted 20 min until no further weight loss was observed in the sample. Then, the sample was again tarred and heated to 800°C at a rate of 10°C/min. The thermogravimetric analysis of the cellulose fibers without the fluorocarbon polymer modifier and the fibers with the modifier containing 5 and 15%, respectively, are shown in Figure 5.

Based on the thermogravimetric analysis, the maximum decomposition rate of cellulose fibers was calculated by Phyris software (version 3.81). The peak of the first derivative calculated from the thermogravimetric curve shows the maximum decomposition rate of the fiber samples. The example of calculation is shown in Figure 6.

The results of the above calculations are shown in Table III.

The maximum decomposition rate temperature is related to the heat resistivity of the samples. According to the results calculated, the addition of fluorocarbon polymer to the fiber material does not influence the heat resistivity of the cellulose fibers. The cellulose fibers without polymeric modifier start to decompose at about 300°C, and the maximum decomposition rate occurs at about 339.2°C. The thermal decomposition of the fibers modified with fluorocarbon polymer also starts at about 300°C, and the maximum decomposition rate occurs between 336.0 and 340.5°C. At first glance, these results seem random and not to display any pattern. The differences between the temperature of decomposition of the samples are not great, and it is somewhat difficult to state that the modifier has any influence on the fibers' heat resistivity. The meaning of the data given in Table III can be easily understood if compared to the mechanical properties of the cellulose fibers. In Figure 7, the mechanical and thermal properties of the fibers
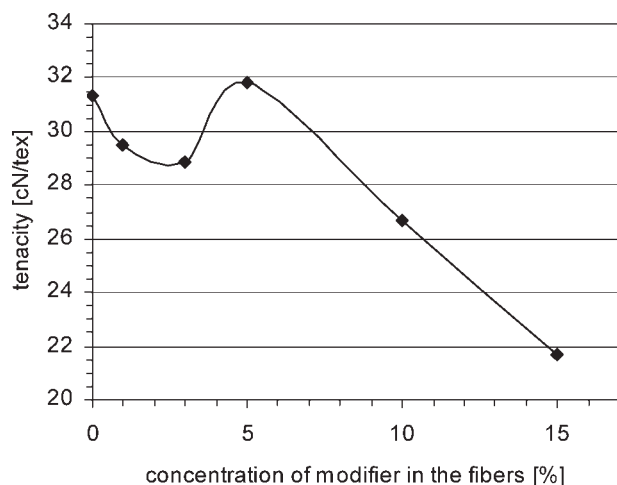

Figure 3 The tenacity of the cellulose fibers versus the concentration of fluorocarbon modifier.
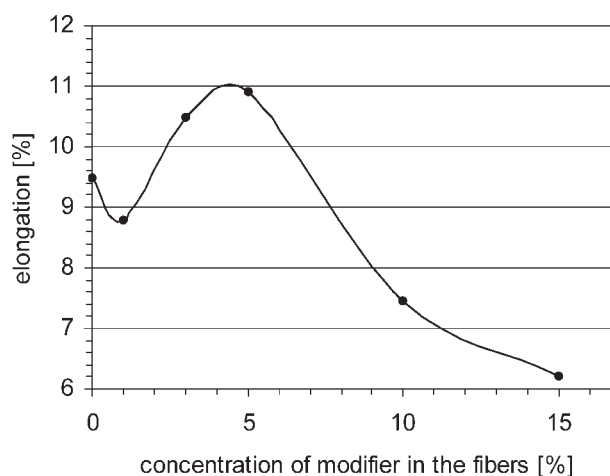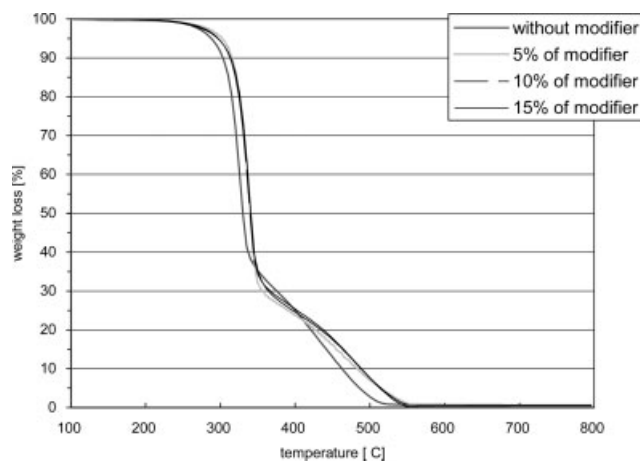

Figure 4 The elongation of the cellulose fibers versus the concentration of fluorocarbon modifier.
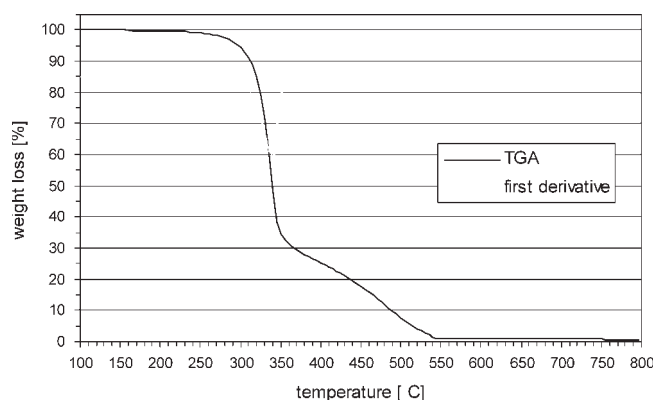
Figure 5 The thermogravimetric analysis of fibers containing fluorocarbon polymer modifier.

The Maximum Decomposition Ratio Temperature for the Cellulose Fibers Modified by the Fluorocarbon Polymer

Concentration of modifier in the fibers (%)	Temperature of maximum decomposition rate (°C)
0.0	339.2
1.0	337.5
3.0	336.0
5.0	340.5
10.0	339.6
15.0	0

obtained are shown on the same chart. According to the data shown in Figure 7, it is clear that in this case the decomposition temperature strongly depends on the structure of the fibers. It seems that the modifier, which should theoretically increase the heat resistivity of the fibers, in fact influences the spinnability of the spinning solution, as well as the fibers' structure. The better spinnability of the spinning solution causes higher macromolecule orientation, which ultimately affects the mechanical properties (higher tenacity) and thermal properties (higher thermal stability).

Differential scanning calorimetry analysis

The cellulose fibers modified by fluorocarbon polymer were examined by means of differential scanning calorimetry (DSC). Thermograms of these fibers are shown in Figure 8. The thermograms for unmodified fibers and cellulose fibers containing modifying polymer are very similar. There is only one endothermic peak, in the region of about 340–450°C, which is
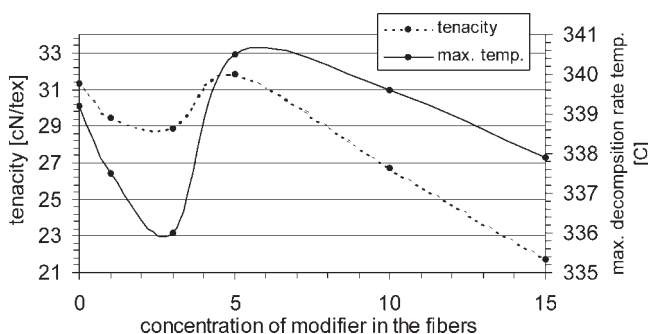
related to the decomposition of the fibers. The value of the decomposition enthalpy and the temperatures of the maximum decomposition ratio are shown in Table IV.

Based on the data presented in Table IV, the graph in Figure 9 was prepared.

As stated earlier, the mechanical properties of the fibers and the properties of the spinning solution, such as spinnability, depend to a great extent on the concentration of the modifier. The results obtained by DSC analysis clearly demonstrated this fact. The value of enthalpy during fiber sample decomposition shows a maximum (the largest peak area) for samples containing about 5% of modifier. Higher decomposition enthalpy suggests a better orientation of macromolecules in the fiber material, which simultaneously effect the mechanical properties positively, such as higher tenacity.

To show how strong the correlation between modifier concentrations, and the fiber mechanical properties and their molecular structure is, Figure 10 was drawn. In this figure, the tenacity of modified fibers and decomposition enthalpy was drawn on the same chart.

The data shown in Figure 10 fully confirm the results shown in Thermogravimetric Analysis section.

Figure 6 The thermogravimetric analysis and the first derivative for fibers containing fluorocarbon polymer modifier (for fibers containing 10.0% of modifier).

Figure 7 Correlation between tenacity and maximum decomposition rate temperature versus the concentration of fluorocarbon modifier.
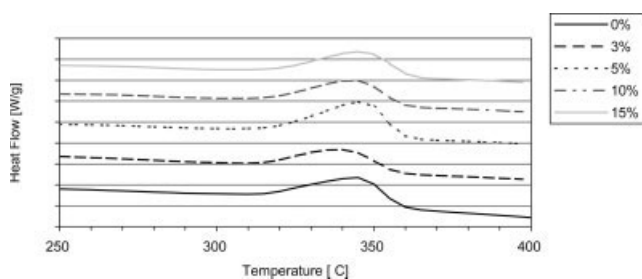
Figure 8 The thermograms of modified cellulose fibers.

Moisture absorption and water retention

The moisture absorption of the fibers obtained at 65% relative humidity was determined according to Polish standard PN-71/P-04635. The fiber samples were stored in an airtight container at the atmosphere of 65% relative humidity for 24 h. The results for moisture absorption are shown in Figure 11.

As can be expected, the addition of hydrophobic modifier caused a significant increase in the hydrophobic properties of the fibers. The cellulose fibers' moisture absorption ability decreased when the concentration of fluorocarbon polymer contents rose. It was observed that the addition of polymer modifier up to 3% w/w caused a relatively significant drop in the fibers' moisture absorption of about 10%. A further increase of the fluorocarbon polymer in the cellulose fibers caused relatively small drop in the moisture absorption. The addition of 15% of modifier causes a drop in the moisture absorption of only about 20%. According to the shape of the curve shown in Figure 11, a further increase of the modifier contents in the fibers will not cause changes in the hydrophobic properties of the fibers. The rather small influence of the modifier on the hydrophobic properties of the cellulose fibers can be explained by the fact that the modifier introduced creates a kind of domain in the fiber material, which will be discussed in the next section (Microscope Examination section). It seems that the hydrophilic properties of the cellulose and cellulose solvent allows a rather small amount of

TABLE IV
The Value of the Decomposition Enthalpy, and the Temperature of the Maximum Decomposition Ratio for Cellulose Fibers Modified by the Fluorocarbon Polymer

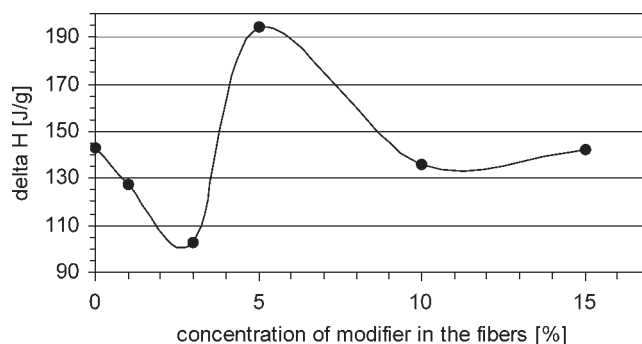| Concentration of modifier in the fibers (%)	Enthalpy (J/g)	Temperature at the peak (°C)
0.0	142.6	343.7
1.0	127.4	341.1
3.0	102.3	340.9
5.0	194.3	346.1
10.0	135.9	344.1
15.0	142.1	345.8

Figure 9 Enthalpy value of decomposition area versus the concentration of fluorocarbon modifier.

the hydrophobic modifier to be homogenized (up to about 3.0% w/w). The modifier at higher concentrations cannot be perfectly mixed to the fiber material and creates longitudinal domains as a separate phase. Probably, only the homogenized part of the modifier significantly changes the properties of the fibers. The nonhomogenized part of modifier creates a separate phase and does not have a big influence on the absorption properties of the whole material. In short, only the homogenized part of the modifier significantly influences the hydrophobic properties of the fibers.

Water retention was measured in accordance with Polish standard PN-72/P-04800. Samples of the fibers were immersed in distilled water containing a surface active agent (Rokafenol N-8 in an amount of 0.1%) for 24 h and then centrifuged off for 10 min at 324 rad/s. The results of retention determination are shown in Figure 12.

The characteristic of the curve of water retention of the modified fibers is in some ways similar to the curve of moisture absorption (Fig. 11). The relatively small amount of hydrophobic modifier present in the fiber material caused a rather significant drop in the
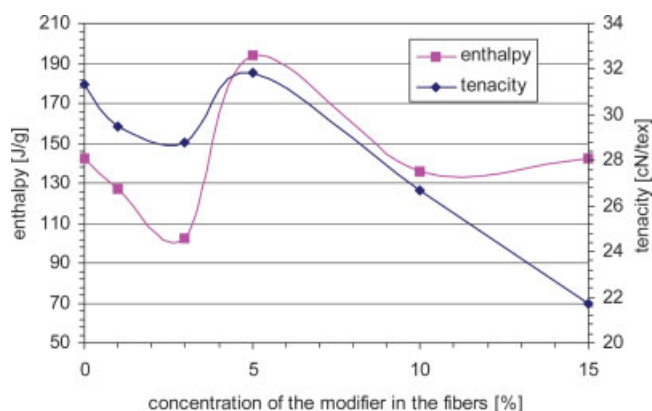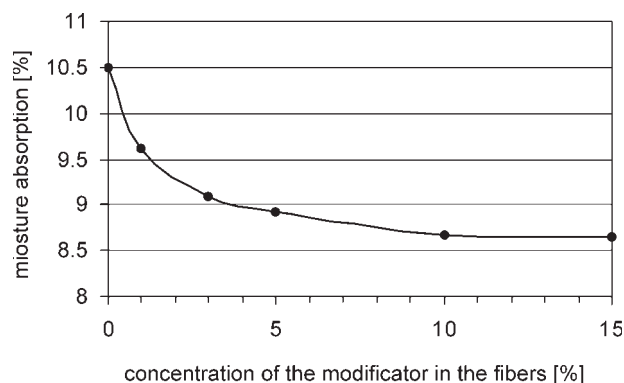

Figure 10 Correlation between tenacity and decomposition enthalpy versus the concentration of fluorocarbon modifier. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

Figure 11 Moisture absorption of modified fibers versus concentration of modifier in the fibers.

water retention of about 10%. Further increase of the modifier contents does not cause any substantial drop in water retention. Those results may suggest that the addition of the modifier up to only 5% has a considerable influence on the internal structure of the fibers and their hydrophobic properties.

Microscope examination

Optical microscope

The fibers obtained were examined by means of optical microscopy. The fibers were cut into sections of about 5 mm in length, placed on a microscopic slide, then immersed in immersion oil and covered with a microscopic cover glass. The picture of the fibers were taken by a digital camera and saved as an image. The pictures of fibers without modifier and with 1, 5, and 15% of modifier are shown in Figure 13.

The cellulose fibers contained no fluorocarbon polymer, are transparent, and show no visible traces of foreign bodies.

The fiber with the addition of the modifier have visible oblong dark shapes, which may suggest the presence of the modifier's domains in the fiber materials. The more modifier the fibers contain, the thicker and more distinct the domains are. It seems that the hydrophobic compound has a limited ability to create a homogenous mixture with hydrophilic polymer, as the cellulose is. Above a certain concentration the modifier cannot be entirely mixed with cellulose, and finally constitutes the system of two separated phases. Because the phases have different optical density, they are easily visible in the optical microscope.

Scanning electron microscope

To examine the fibers' structure more precisely, scanning electron microscopy was applied. In Figure 14, the SEM images of modified and unmodified fibers are shown.

The cross-sections of cellulose fibers shown in Figure 14 have a regular round shape, similar to those of synthetic and polynosic fibers. However, the morphology of the fibers is not considerably different, although some changes in the topography of the cross sections of the fibers can be seen. In Figure 14(b), the small shapes standing out from the surface of the fibers can suggest the presence of fibrils or domains, which create a modifier that is not fully mixed. In Figure 15, the cross section of the fibers containing 15% of fluorocarbon polymer is shown. The area where the fibrous structures are present is marked with a white circle.

It seems that too high a concentration of the modifier changes the structure of the fibers and negatively influences its mechanical properties. The cross sections of the cellulose fibers containing 15% of fluorocarbon modifier are shown in Figure 16.

The relatively high concentration of the modifier causes the creation of bulk bodies, which apparently constitute a separate phase in the fiber material. In the cross sections of the fibers, which were mechanically torn off from the bulk structures, their round concave traces are visible on the SEM images. The pictures also show that the bulk structures are rather weakly bonded to the cellulose matrix, which finally causes a decrease in the tensile strength of the fibers.

For the modified cellulose fibers, SEM images of fibers' surface were taken. They are shown in Figure 17.

For the fibers containing a relatively small quantity of modifier, the surface is smooth and no defects are visible. The more modifier the fibers contain, the more defects are visible on the surface of the fibers. The surface defects on the fibers can be explained by the presence of domains of the modifier in the spinning fibers. In the first step of the spinning process, the cellulose solution is extruded from the holes of the spinneret and drawn out. During this process, the modifier domains are created. Relatively thick and not yet coagulated filaments are immersed into the coagulation bath when the solvent (NMMO) is removed. At that time, the continuous drawing and
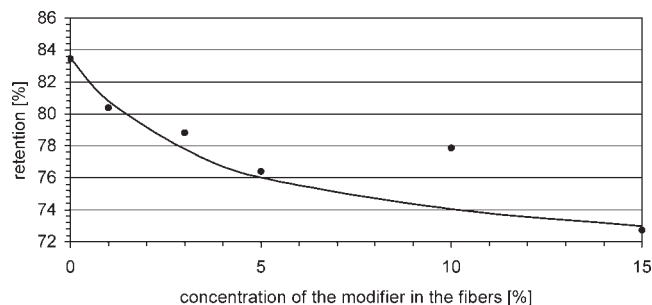
Figure 12 Water retention of modified fibers versus concentration of modifier in the fibers.
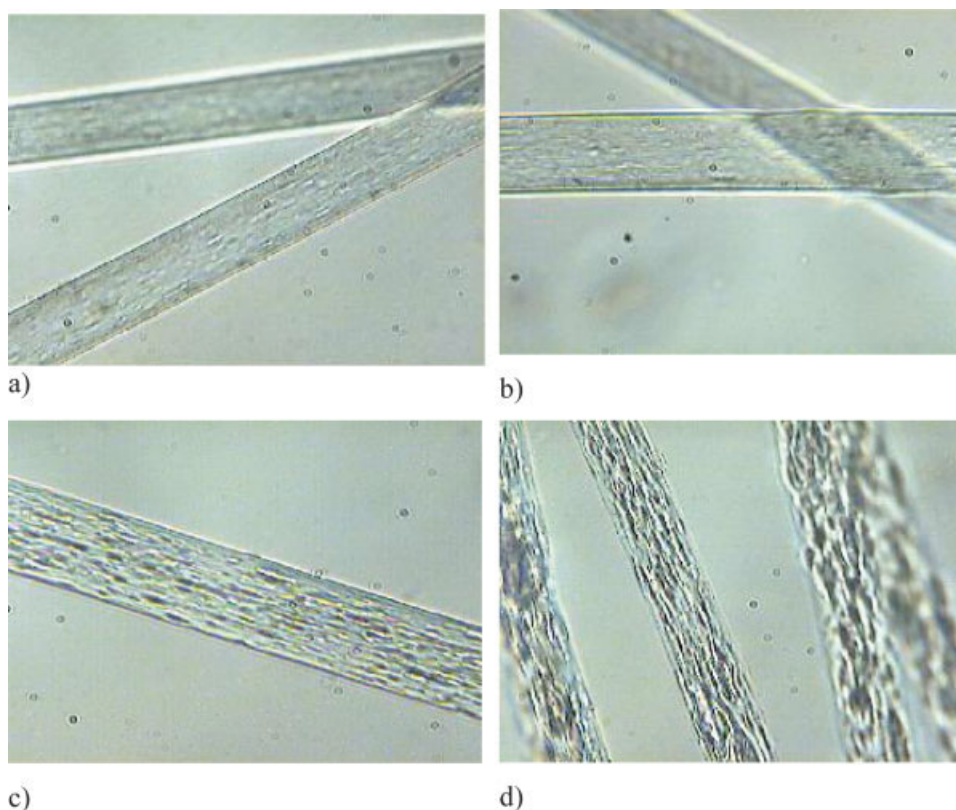
Figure 13 Images of the cellulose fibers by optical microscopy: (a) cellulose fibers without modifier, (b) cellulose fibers with 1% of modifier, (c) cellulose fibers with 5% of modifier, and (d) cellulose fibers with 15% of modifier. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]
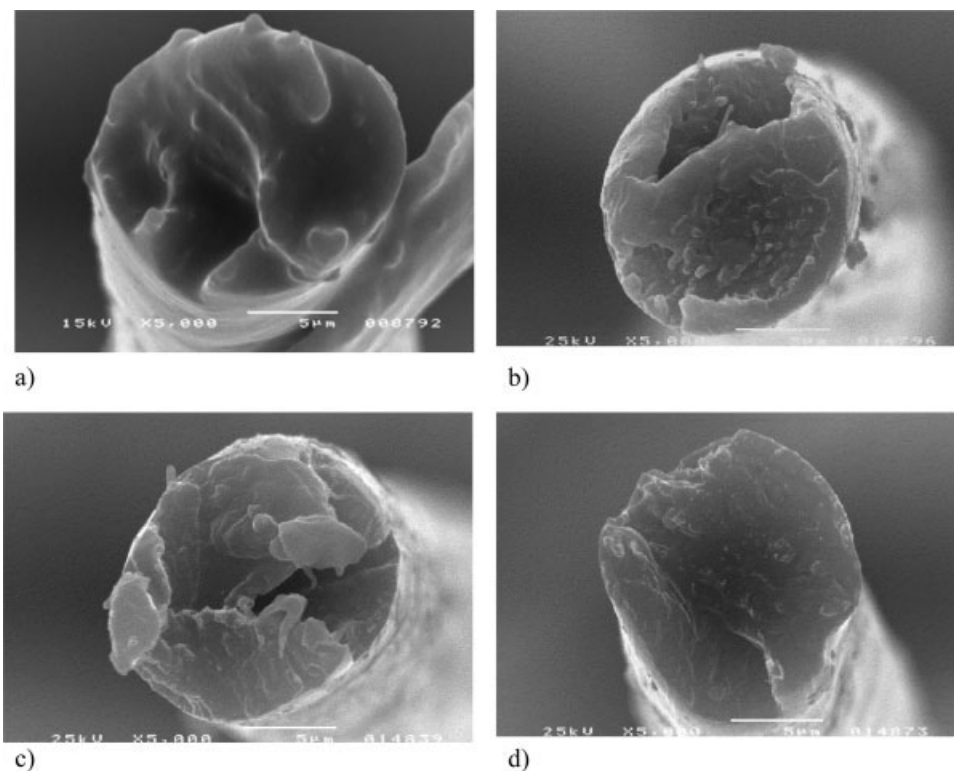
Figure 14 Cross-sections of cellulose fibers: (a) cellulose fibers without modifier, (b) cellulose fibers with 5% of modifier, (c) cellulose fibers with 10% of modifier, and (d) cellulose fibers with 15% of modifier.
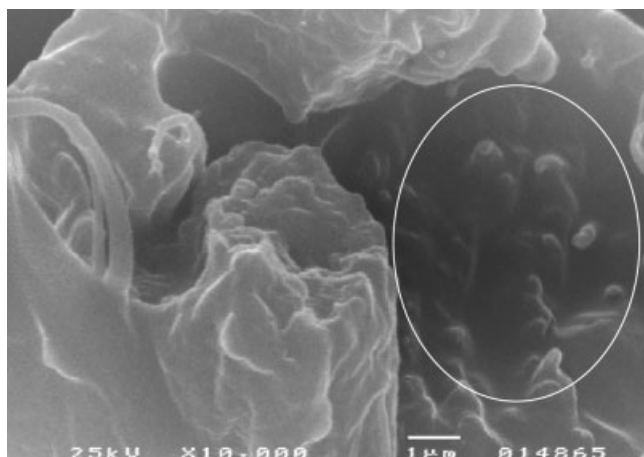
Figure 15 Cross-section of the fibers containing 15% of fluorocarbon modifier.

the process of coagulation cause the diameter of the fibers to decrease. The shrinking of the volume of the fibers causes a compression of the domains. It may happen that the domains lying just under the fiber surface are squeezed by the shrunken polymer matrix, which finally brings about the formation of defects on the surface of the fibers. The process of the formation of defects is shown in Figure 18.

Fiber fibrillation tendency test

It is well-known that the cellulose fibers obtained by the NMMO method have a tendency to fibrillation.[21,22] To check if the addition of fluorocarbon polymer has any influence on the tendency to fibrillation, "Shake Tests"[24] were carried out. The test consists of vigorous shaking for 9 h of eight elementary fibers with a length of 20 mm in small bottles, 20 mL in volume, containing 4 mL of distilled water. After that, the fibers were observed under a microscope to evaluate the resultant fibrillation. The number of fibrils at the definite fiber length and their appearance were taken into account as criteria for the fibrillation

of the fibers. The degree of fibrillation is shown as a number between 0 and 6. The higher the number, the higher the tendency to fibrillation.

Some typical images of the cellulose fibers after the shaking test are shown in Figure 19.

Based on microscope images, the degree of fibrillation of modified fibers were estimated. The results are shown in Table V.

However, the optical way of determining the degree of fiber fibrillation is rather subjective, but the data shown in Table V and the images of the fibers presented in Figure 16 suggest that the fibers containing fluorocarbon polymer as a modifier have a lower tendency toward fibrillation than the unmodified cellulose fibers. The lower tendency may be caused by the fact that the modifier has some crosslinking properties. The lowest fibrillation tendency is shown in the fiber containing 5% of fluorocarbon modifier, which again confirms the assumption of the optimal concentration of the modifier in the fibers.

CONCLUSIONS

Cellulose fibers modified with the fluorocarbon polymer were prepared. The concentration of modifier in the cellulose fibers varied from 1.0 to 15% w/w. It seems that the NMMO process is very suitable for preparing cellulose fibers modified with this kind of modifier. The elemental analysis showed that at least 75% of the entire amount of the polymeric modifier introduced at the beginning of the cellulose dissolution process remains in the cellulose fibers.

The fluorocarbon polymer in cellulose fibers causes a decrease in the tenacity and elongation of the fiber. Fibers containing 15% of modifier have about 30% lower tenacity than cellulose fibers without the modifier. The presence of 15% of modifier also caused a drop of about 37% in the elongation of the cellulose fibers.

However, the modifier is a fluorocarbon polymer and has no significant influence on the fibers' heat resistance properties. The fibers contained 15% of
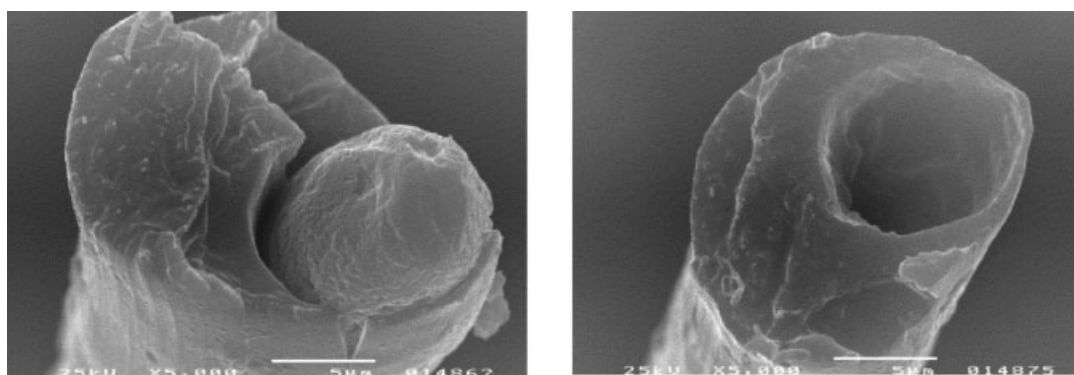
Figure 16 SEM images of the fibers containing 15% of fluorocarbon modifier.
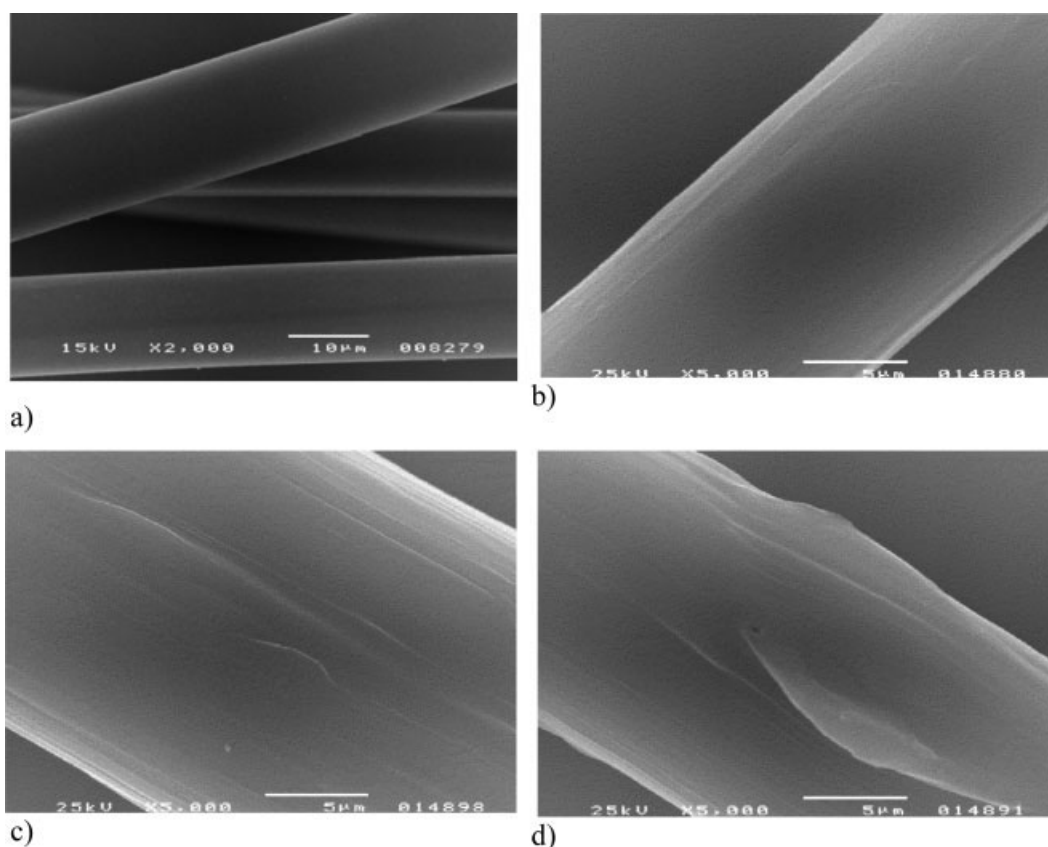
Figure 17 The SEM images of the surface of cellulose fibers: (a) cellulose fibers without modifier, (b) cellulose fibers with 5% of modifier, (c) cellulose fibers with 10% of modifier, and (d) cellulose fibers with 15% of modifier.

polymer, which decomposed at almost the same temperature as the cellulose fibers without modifier. The maximum decomposition rate temperature of the fibers is strongly correlated with the spinning dope properties and with the spinning conditions.

The concentration of the polymeric modifier influences the spinning solution's properties. About 5% of modifier causes better spinnability, which is reflected in the mechanical properties of the fibers obtained.

However, the modifier has hydrophobic properties; adding more than 5% w/w does not cause any significant drop in either moisture absorption or water retention.

In the cellulose fibers containing over 3% of fluorocarbon modifier, the domain structure is visible.

The SEM examinations demonstrated the presence of the domain structures in the modified fibers. The relatively low tenacity of the fibers containing a higher concentration of the modifier may occur not only because the modifier is a material showing no spinnability properties, but also because the fluorocarbon polymer creates bulk structures that are rather weakly bonded to the cellulose matrix.

It is well-known that cellulose fibers obtained by the NMMO method have a tendency toward fibrillation. The presence of the modifier in the fiber material decreases theirs feature. According to the shake test, the lowest fibrillation tendency is found in the fibers containing about 5% w/w of the fluorocarbon modifier.

All of the results presented in this article suggest that the optimum concentration of the fluorocarbon modifier is about 5% w/w. It seems that the addition of about 5% w/w of modifier significantly improved the
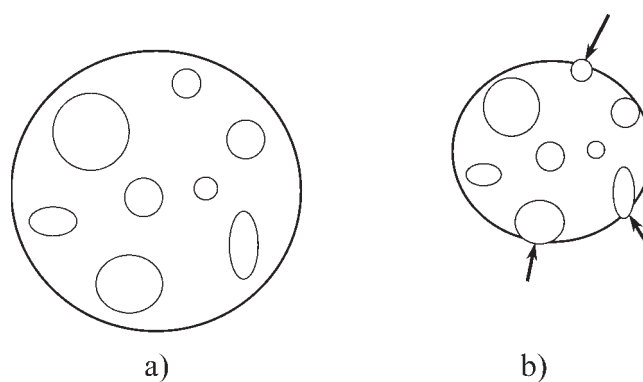
Figure 18 Schematic of the defects formation on the surface of the fibers: (a) cross-section of noncoagulated filament with modifier domains and (b) cross-section of coagulated fiber (dotted shapes are the domains and arrows show the defects points).
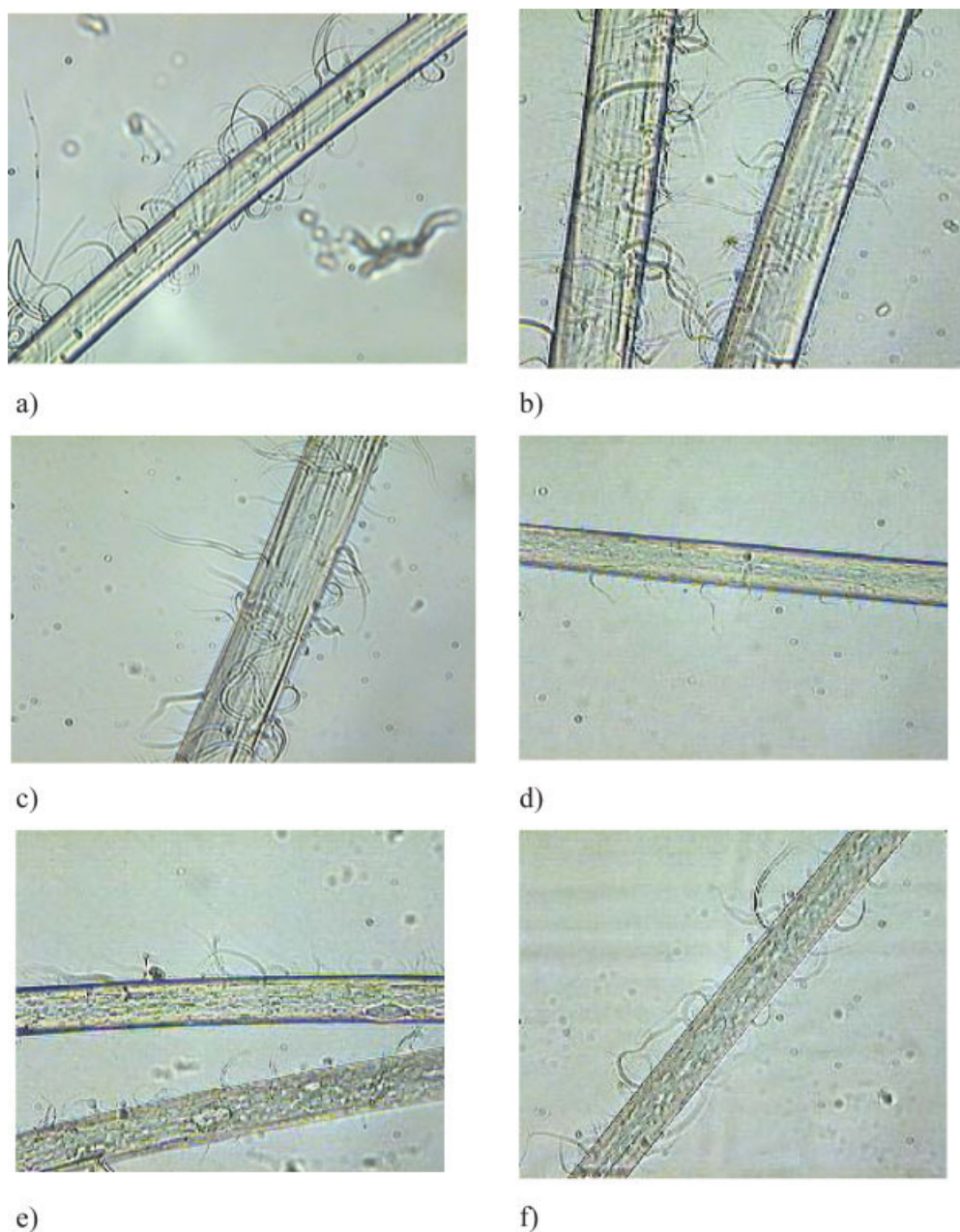
Figure 19 Optical microscope images of the cellulose fibers after shaking test: (a) cellulose fibers without modifier, (b) cellulose fibers with 1% of modifier, (c) cellulose fibers with 3% of modifier, (d) cellulose fibers with 5% of modifier, (e) cellulose fibers with 10% of modifier, and (f) cellulose fibers with 15% of modifier. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

properties of the cellulose fibers. From the application point of view, using a concentration of the modifier higher than 5% w/w is pointless.

TABLE V
The Fibrillation Degree for Modified Cellulose Fibers

Concentration of modifier in the fibers (%)	Fibrillation degree
0.0	5.0
1.0	4.0
3.0	3.0
5.0	1.5
10.0	3.0
15.0	4.0

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