Composite fibres based on cellulose and vinyltriethoxysilane: preparation, properties and carbonization

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Abstract. For the first time the composite fibers based on cellulose with additives of vinyltriethoxysilane (VTEOS) have been obtained. The choice of the additive was justified by the chemical structure of the VTEOS, namely the Si-C links content and the low C/O ratio. Composite fibers were prepared from solid phase pre-solutions of cellulose with VTEOS in N-methylmorpholine-N-oxide (NMMO). An investigation of the rheological behavior of the filled cellulose solutions with VTEOS showed a slight effect of the additive on the viscosity properties of the system. Introduction of 5% of VTEOS to cellulose does not lead to significant structural changes and, as a result, mechanical properties of the fibers. The thermal behavior of composite fibers differs from cellulose fibers.

1. Introduction
Carbon fibers (CF) based on cellulose, remain irreplaceable to date due to a number of their unique functional properties, for example, small values of the thermal expansion coefficient. Improvement of the carbonization process includes using as additives chemical reagents of various types (organic, inorganic and silicon- or halogen-containing compounds, metal salts, etc.) affecting the carbonization process, i.e., playing a role of catalyst [1].

Along with the change in the mechanism of carbonization process, which manifests in the change of the DSC traces, the additives influence (as a rule, increase) the value of the carbon residue at producing CF.

From this point of view the additives work as fire retardants, and silicon-containing compounds are popular for this aim [2-4]. Silicon flame retardants are applied to the precursor fibers by impregnation. Unfortunately, this method does not allow to reach a uniform distribution of the additive in fibers – the surface is enriched, but the volume is depleted with active substance. As an alternative method to achieve a good distribution of the additive in the fiber volume is it introducing into the spinning solution (the dope) [5].

Since the rayon production in many countries is diminished because of ecological problems, the NMMO process, where the of cellulose dissolves in direct solvent - N-methylmorpholine-N-oxide (NMMO) becomes more and more popular [6]. That is why we have used these solutions for spinning cellulose fibers of Lyocell type.

Introduction of tetraethoxysilane (TEOS) into cellulose solutions in NMMO was proposed by our group and described in [7]. The viscosity of such solutions is slightly differed from that, typical for the neat cellulose solutions. This renders it possible to obtain composite fibers in conditions, previously...
defined for cellulose solutions. When introducing up to 10% TEOS into a cellulose matrix strength and elongation at break of fibers do not change practically, while the modulus of elasticity increases on 20-30%. It allowed us to conduct the further thermal treatment of composite precursors and to obtain carbon-silicon carbides fibers [8].

Compared with TEOS, vinyltriethoxysilane (VTEOS) is characterized by the presence of one Si-C bond and only three Si-O bonds that allows us to expect that lower oxygen content in precursor fibers could lead to increase of carbon yield at thermolysis of composite fibers due to formation of silicon carbide. Thus, the aim of this work consists in preparing composite fibers based on cellulose and VTEOS solutions in NMMO and studying their structure and properties.

2. Experimental

2.1. Materials
Cellulose with DP = 600 was received from Baikal Pulp and Paper Mill (Russia) (H₂O ~ 8%, alpha cellulose content not less than 94% (GOST 6840-78). N-methylmorpholine-N-oxide (MMO) (T_m.p. 120-160°C, H₂O <10%) were supplied by Demochem (China). Triethoxyvinylsilane (VTEOS) (H₂C = CHSi(OCe₂H₅)₃) (ID 24850510) and Propylgallate (ID 329757396) were from Sigma-Aldrich (USA).

2.2. Preparation of composite fibers
Composite fibers based on cellulose with VTEOS were spun by a dry-wet method on laboratory unit Rheoscope 1000 capillary viscometer (Ceast, Italy) from solutions prepared via solid-phase treatment of components according to the procedure described in [7]. The diameter of the capillary used was 1 mm, and the length-to-diameter ratio was 40.

2.3. Characterization
X-ray diffraction studies of the obtained fibers were carried out at room temperature in an apparatus with rotating copper anode (Rigaku, Japan) in the transmission mode. The beam radiation was CuKα with a wavelength λ = 0.1542 nm. To produce equatorial X-ray diffraction patterns, the parallel folded filaments (~ 100) were used. The morphology of the fibers was studied by the scanning electron microscope JSM U-3 (JEOL, Japan). The mechanical properties of the fibers were determined in Instron 1122 tensile machine (UK) on a 10 mm basis at a strain rate of 10 mm/min. Thermal behavior of the fibers was investigated on a TGA/DSC1 thermal analysis instrument, Mettler Toledo (Switzerland). The measurements were carried out in alumina crucibles of 70 μl in the temperature range from 30 to 1000°C at a heating rate of 10 K/min. The inert gas consumption (argon) was 10 cm³/min. Carbonization of filaments was carried out in the operating cell of the TMA 402 F1 Hyperion device for thermal mechanical analysis (Netzsch, Germany) up to 1200°C.

Content of silicon in the samples was determined using a multielement CHNS/O analyzer "Thermo Scientific Flash 2000” (USA) and transmission electron microscopy Osiris (FEI, USA).

3. Results and discussion
The equatorial diffractograms of cellulose and composite fibers obtained in the "transmission" mode at room temperature are shown in Figure 1.

On both diffractograms, peaks are observed in the regions 2θ ~ 12-13° and ~ 20.5°, i.e. inherent for cellulose II. Change in the intensity ratio of the peaks belonging to cellulose and composite fibers indicates on of a less ordered structure in composite fibers.

The morphology of composite fibers does not differ from cellulose fibers (Figure 2).
Figure 1. Equatorial diffractograms of cellulose (1) and composite fibers (2).

Figure 2. Micrographs of cellulose (a, b) and composite fibers (c, d) containing 90% cellulose and 10% VTEOS, cross-sections (a, c) and surface (b, d).

As can be seen from micrographs, the addition up to 10% VTEOS leads to preparing fibers with a circular cross-section and a smooth defect-free surface of fibers. The average fiber diameter is 15-20 μm.

Mechanical properties of composite fibers revealed that with increase in the VTEOS content to 10%, the strength is slightly decreased (~ 5%), and the values of the elongation at break fell by half, and values of the elastic modulus did not change (Table 1).
Table 1. Mechanical properties of cellulose and composite fibers.

|                | Ø, μm | σ, MPa | ε, % | E, GPa |
|----------------|-------|--------|------|--------|
| 100% cellulose | 14-20 | 570-610| 10-12| 11-12  |
| 95% cellulose + 5% VTEOS | 11-13 | 460-510| 6-8  | 11-12  |
| 90% cellulose + 10% VTEOS | 9-11  | 460-550| 6-8  | 11-12  |

The composite precursor fibers were processed into carbon fibers. The morphology of the obtained carbon fibers obtained at a temperature treatment up to 1000°C is shown in Figure 3.

Figure 3. Micrographs of carbon fibers obtained from precursors containing 90% cellulose and 10% VTEOS, obtained by heat treatment in argon atmosphere up to 1000°C at different magnification.

The surface of carbon composite fibers is relatively smooth, but there exists "craters" of a small size (Figure 3). The cross-sectional pattern is uniform. The average diameter of the carbon fibers is ~ 6-9 μm. The distribution of the chemical elements in the resulting carbon fibers is shown in Figure 4.

Figure 4. Micrographs of carbon fibers after thermolysis at 1000°C (a) and distribution of elements: C (b), O (c), Si (d) in these fibers.

It is seen from the micrographs (Figure 4) that C, O, Si are evenly distributed, and their absolute values were determined by TEM method and shown in the histogram (Figure 5).

Char yield obtained by heat treatment of composite precursor fibers up to 1000°C in 2-3 times higher than for neat cellulose fibers, meanwhile it first increases at small additive content, but further decreases. The observed decrease in the carbon residue at high level of additive is possibly associated with an increase in the oxygen concentration in the precursor fibers.
Content, %

97,5%
2,1%
0,4%

SiOC

Figure 5. The content of C, O, Si in carbon fibers obtained from a precursor containing 95% cellulose and 5% VTEOS.

5. Conclusion

The introduction of VTEOS into the cellulose matrix at the stage of solution preparation renders it possible to obtain composite precursors with a good distribution of silicon in the volume of the fiber. The mechanical properties of the obtained composite fibers and their morphological quality are slightly differ from cellulose fibers, that allows to process them into carbon fibers with uniform distribution of chemical elements.

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