Study of the composition of a hydrophobic coating obtained by a plasma chemical deposition from the gas phase on the surface of textile material

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Abstract. In this work, a hydrophobic non-continuous granular coating with a thickness of no more than 1-3 microns, obtained by modifying textile materials with nonequilibrium low temperature plasma (NLTP) in argon-acetylene medium (70:30), was investigated. As a result, the obtained coating is a mixture of hydrocarbons, mainly paraffins, as well as unsaturated hydrocarbons formed during the polymerization and decomposition of acetylene in the presence of copper, such as alkenes, polyacetylene isomers and others, which contribute to an increase in waterproofing properties.

1. Introduction

Today, the process of waterproofing textile materials is of great interest both from a scientific and practical point of view. To make textile materials of sustainable hydrophobicity, it is necessary to create a new surface with a significantly lower surface energy on the outer surface of the fibers forming them. In practice, the reduction of the surface energy of a textile material is most often carried out by applying water-repellent agents from emulsions or dispersions (fluoropolymers). However, the use of fluoropolymers is limited due to undesirable effects on the properties of the finished product, a high degree of leachability and toxicity [1].

The use of working media in the supercritical fluid state is a new and little-studied direction of hydrophobization of textile materials. Despite the versatility and low cost of supercritical technologies, as well as the creation of ultra- (θ > 1200) and superhydrophobic (θ > 1500) surfaces of textile materials [2], it is technically quite difficult to ensure a pressure of 10 MPa in large scale production.

An alternative method of waterproofing textile materials is an environmentally friendly plasma technology. It is known [3-5] that the processing of polymeric materials in the medium of hydrocarbon gases leads to an increase in their hydrophobic properties. The authors of afore mentioned works associate an increase in the hydrophobicity of the surfaces of materials when modifying propane-butane in plasma with the formation of grafted methyl and ethyl groups of radicals on the surface, the
formation of nanoscale carbon layers (10–50 nm thick) and blocking the polar groups of the material. However, a detailed study of the obtained nanoscale layers of carbon has not been conducted. Therefore, on the basis of previous studies [6, 7] on the formation of a hydrocarbon coating on the surface of textile materials in argon-acetylene, the problem of studying the composition and nature of this coating seems to be relevant. The purpose of this work is to identify the products of plasma-chemical deposition from the gas phase (PCVD – Plasma chemical vapor deposition) on the surface of textile materials.

2. Materials, methods and equipment
The objects of study were selected textile materials produced by Ltd. «TK Tchaikovsky Textil», Tchaikovsky city: fabric art. 80304 Climate 150 RS (100% polyether) with oil-water-repellent (OWR) impregnation and fabric art. 87015 Climate 260 (78% polyester, 22% viscose) with water-repellent (WR) impregnation.

The modification was carried out in an experimental high-frequency condensive complex plasma setup, described in detail in the work [8]. The mode of plasma modification was regulated by changing the parameters within the following limits: gas consumption (G) 0–0.04 g/s, voltage at the anode of the generator lamp (Ua) 3–7 kV, working pressure in the discharge chamber (P) 26.6 Pa; generator frequency (f) 13.56 MHz, processing time (τ) 1–10 min. A mixture of argon and acetylene in the ratio of 70:30 was used as a plasma-forming gas.

After modification of polyester textile materials by a non-equilibrium low-temperature plasma (NLTP) in argon-acetylene medium (70:30), a coating was formed on their surface.

Visualization of the coating obtained on the surface of the fibers of the tissues was carried out using an Olympus LEXT OLS 4000 confocal laser scanning 3D microscope.

The composition of the coating obtained on the surface of the fibers of fabrics was determined by the method of IR Fourier spectroscopy using an FSM 1202 spectrometer from the company «Infraspek» in the range of wave numbers 500–4000 cm⁻¹. The resulting coating was removed from the surface of the tissues and tableted with KBr [9]. A pressed KBr powdered disc was used as a reference sample.

3. Results
The change in the microstructure of the fibers of the studied textile materials after NLTP in argon-acetylene is shown in Fig. 1.

![Figure 1. CLSM (Confocal Laser Scanning Microscop) images of materials surfaces: art. 80304 Climate 150 RS (a) of the original sample and (b) the modified sample in the NLTP (mode: Ua = 5 kV, τ = 7 min, P = 26.6 Pa, GAr/C2H2(70:30) = 0.04 g/s), art. 87015 Climate 260 (c) of the original sample and (d) of the modified sample in the NLTP](image)

On microphotographs (Figure 1 b, c) of tissue fibers after NLTP modification, a coating can be observed. PCVD-coating has a rather non-continuous structure with a grain size of no more than 1–3 microns.

The study of the nature of this coating was carried out using IR Fourier spectroscopy. The results are presented in Fig. 2.
The coating obtained in acetylene media is a mixture of hydrocarbons, which demonstrate the following absorption bands on the spectrum (Fig. 2):
- the absorption band in the range of 3310–3200 cm⁻¹, corresponding to the stretching vibrations of the ≡C–H groups;
- split absorption band 3000–2840 cm⁻¹ (νas CH₂), corresponding to the stretching vibrations of the –CH₂ groups;
- band 2875 cm⁻¹ (νs CH₃), corresponding to the stretching vibrations of the CH₃ group;
- the absorption band in the range of 1580–1720 cm⁻¹, corresponding to the stretching vibrations of the C=CH group;
- bands 1377 cm⁻¹ (δs) and 1454 cm⁻¹ (δas) refer to deformational vibrations of the CH₃ group;
- bands in the range of 650–1000 cm⁻¹ relate to non-plane deformation vibrations C–H.

Thus, it can be assumed that the formation of a coating in argon-acetylene medium occurs according to the following mechanisms:

a) the formation of cuprene from acetylene or its aromatic derivatives when heated in an ionized medium in the presence of copper electrodes:

\[ \text{C}_2\text{H}_2 + \text{Cu} \rightarrow \text{H} \quad \text{C} \equiv \text{C} \equiv \text{C} \equiv \text{H} \quad \text{Ar} \]

where n is not more than 10, because the coating formed is non-continuous;

b) at low pressures, in the process of decomposition of acetylene, mono-radicals arise, which contribute to the development of the chain process with the highest rate of passing through the reactions:

\[ \text{C}_2\text{H}_2 \rightarrow \hat{\text{CH}} \rightarrow \hat{\text{CH}} \]

this also occurs, when the chain is developed in a following way:

\[ \text{CH} = \hat{\text{C}} + \text{C}_2\text{H}_2 \rightarrow \text{CH} = \hat{\text{C}} + \text{H} \]

\[ \text{CH} = \hat{\text{C}} + \text{C}_2\text{H}_2 \rightarrow \text{CH} = \hat{\text{C}} + \text{H} \]

\[ \text{H} + \text{C}_2\text{H}_2 \rightarrow \text{H}_2 + \text{CH} = \hat{\text{C}} \]

c) hydrogenation of acetylene to form saturated hydrocarbons

\[ \text{C}_2\text{H}_2 \quad 2\text{H}_2 \rightarrow \text{C}_2\text{H}_6 \]

and this is reflected in the IR spectra of the substance obtained.

Based on the experimental data obtained, it can be assumed that the coating is a mixture of hydrocarbons, mainly paraffins, as well as unsaturated hydrocarbons formed during the polymerization and decomposition of acetylene in the presence of copper, such as alkenes, polyacetylene isomers and others that contribute to an increase in waterproofing properties.
4. Conclusions
Thus, as a result of modification of polyether materials by NLTP in argon-acetylene medium (70:30), a PCVD-coating of acetylene decomposition products and polymerization is formed on the surface of fibers of fabrics. This non-continuous coating is formed by hydrophobic hydrocarbon substances, presumably alkanes, alkenes, polyacetylene isomers, and others.

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