ISSN 1070-3632, Russian Journal of General Chemistry, 2012, Vol. 82, No. 13, pp. 2259–2269. © Pleiades Publishing, Ltd., 2012.
Original Russian Text © N.P. Prorokova, T.Yu. Kumeeva, D.P. Kiryukhin, L.N. Nikitin, V.M. Buznik, 2011, published in Rossiiskii Khimicheskii Zhurnal, 2011, Vol. 55, No. 3, pp. 14–23.

Imparting Enhanced Hydrophobicity to Polyester Fabrics: Formation of Ultrathin Water-Repelling Coatings on the Fiber Surface

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Received July 21, 2011

Abstract—A new technology for hydrophobization of synthetic fiber materials was described. This technological approach is based on formation of nanosized fluoropolymer coatings from solutions of low-molecular-weight fraction of ultradispersed polytetrafluoroethylene and tetrafluoroethylene telomers. The mechanism of formation of protective coatings was described, and the properties of polyester materials thus modified were presented.

DOI: 10.1134/S1070363212130130

INTRODUCTION

The Development Strategy for the Chemical and Petrochemical Industries of Russia till 2015 sets before the chemical industry a task to nearly fivefold increase the production of chemical fibers while significantly expanding their assortment. The strategy envisages "the development of nanotechnologies and their increased use for preparation of materials with special performance characteristics" [1]. With a view to achieving these goals, active research work is currently under way, aimed at production of fibrous materials, in particular, synthetic, which will combine a number of special consumer characteristics.

Modification of conventional synthetic fibers presents a difficult task, because the main fiber components (polyester, polypropylene) are distinguished by high chemical inertness and dense structure. Therefore, great emphasis is placed on approaches to fiber modification based on formation of nanofilms on the surface of fibrous materials. In this context, clearly important is the nature of the modifying substance whose role can be played, e.g., by polytetrafluoroethylene possessing a number of unique characteristics: excellent chemical resistance, high hydro- and liophobicity, record-low friction coefficient, high climatic resistance, good antiadhesion properties, aging resistance, nontoxicity, and biocompatibility [2]. At the same time, chemical inertness, nonsolubility, and poor adhesion properties substantially complicate deposition of polytetrafluoroethylene onto various surfaces.

The primary of objective of textile modification is to impart water repellent properties (hydrophobic finishing) to textile materials, while maintaining the air (water vapor) permeability [3], which effect is achieved via formation of a coating characterized by low surface tension energy. The main indicator of hydrophobicity of materials is the contact (wetting) angle θ which exceeds 90° in the case of hydrophobic materials. The focus of special researchers' attention is on highly hydrophobic materials (ultrahydrophobic, $\theta > 120°$, and superhydrophobic, $\theta > 150°$) [2, 4, 5]. The surface energy of fabrics can be reduced by treating with hydrophobizing agents among which

fluorinated hydrocarbons exhibit the highest efficiency [3, 6]. These agents are deposited onto fibrous materials from emulsions or suspensions. However, the resultant coatings get contaminated with trace amounts of emulsifiers and, moreover, exhibit insufficient stability under conditions of use.

The Institute of Solution Chemistry, Russian Academy of Sciences, developed new procedures for surface modification of synthetic fabrics, which are free from the above-mentioned shortcomings. These procedures make use of materials and techniques facilitating the deposition of fluoropolymer coatings [7–9] (developed by the Fluoropolymer Materials and Nanotechnologies Consortium). This concerns, in particular, the technology of dissolution of the low-molecular-weight fraction of ultradispersed polytetrafluoroethylene powder in supercritical carbon dioxide [10–12] and that of preparation of tetrafluoroethylene telomers in acetone [12–14]. Due to formation of coatings from solutions rather than from emulsions or suspensions, these technologies avoid the above-mentioned shortcomings.

Here, we report on a study concerned with modification of polyester fabric. Polyester fiber is known to be hydrophobic, but fabrics manufactured thereof have an intricate capillary-porous structure and do not possess hydrophobic properties: Fluid droplets getting thereon are instantly absorbed by inter-fiber spaces. Hence, it seems appropriate that a woven material, rather than an individual fiber, be subjected to modification treatment.

Coating Deposition from a Solution of Low-Molecular-Weigh Ultradispersed Polytetrafluoroethylene in Supercritical Carbon Dioxide

One of the procedures proposed for hydrophobization of polyester textile materials is that based on formation of coatings from solutions of low-molecular-weight ultradispersed polytetrafluoroethylene in supercritical carbon dioxide.

Supercritical carbon dioxide is a gas having the density of a liquid though a much larger coefficient of diffusion of the molecules. Our choice of supercritical carbon dioxide as the medium for hydrophobization of the fabrics was dictated by a set of unique properties it possesses: high dissolving and transport characteristics, complete removability from the material upon completion of the process, and low critical parameters, coupled with relative inertness [15–18]. Supercritical carbon dioxide provides for high solubility of hydrophobic agents and absolute wetting of the surface of hydrophobic polymer materials and promotes swelling of polyester fibers.

As hydrophobizing agent served a Forum trademark ultradispersed polytetrafluoroethylene powder developed by the Institute of Chemistry, Far-Eastern Branch, Russian Academy of Sciences. The preparation procedure for this product is based on thermal gas-dynamic decomposition of polytetrafluoroethylene waste accumulated at industrial facilities [19, 20]. This material consists of low- and high-molecular-weight fractions, of which the former comprises mainly 13–16 units [21], and specifically this fraction dissolves in supercritical carbon dioxide [7, 20–22].

Deposition of a low-molecular-weight polytetrafluoroethylene film onto the polyester fabric was carried out at varied pressure and temperature during different treatment times, via decreasing the solubility of the low-molecular-weight fraction of the polymer in supercritical carbon dioxide with decreasing temperature and pressure [7, 23].

To confirm the formation of films on the fabric surface and to gain insight into the composition and structure of the resulting coating, we applied a set of analytical methods [IR spectroscopic (MATR), X-ray diffraction, energy dispersive, gravimetric, elemental, and thermal analyses).

The IR spectra of the treated polyester fabric contain bands near 1210 and 1150 cm^{-1}, characteristic for stretching vibrations of CF_2 groups [10, 12]. These are the main bands in the IR spectrum of Forum [20, 24], and they directly confirm the presence of the fluoropolymer on the fabric surface.

Figure 1 shows the X-ray diffraction patterns of Forum, as well as of the fibers of the initial and treated polyester fabrics [10, 12]. In general, the X-ray diffraction patterns of the fabric did not change under exposure to supercritical carbon dioxide (curves *2* and *3*). The fabric treated with Forum in supercritical carbon dioxide (curve *4*) exhibits a reflection at $2\theta = 18°$, which is the main reflection observed in the diffraction patterns of Forum (curve *1*). The appearance of this reflection also suggests formation of a polytetrafluoroethylene coating on the fiber surface.

The EDX (Fig. 2), gravimetric, and elemental analyses showed that the fabric treated under the

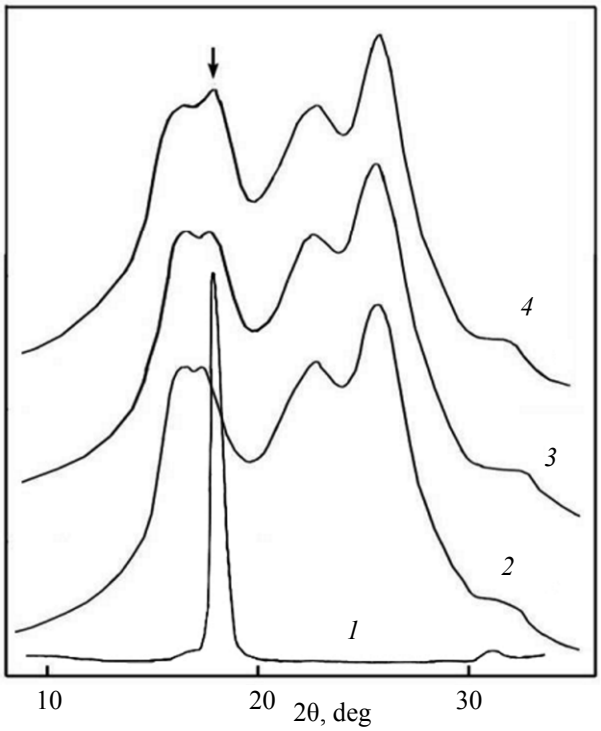

Fig. 1. X-ray diffraction patterns of the polyester fabric fibers and Forum agent [6, 8]: (*1*) Forum agent, (*2*) untreated fabric, (*3*) fabric upon exposure to supercritical carbon dioxide (50 MPa, 90°C, 60 min), (*4*) fabric treated with a Forum solution in supercritical carbon dioxide (50 MPa, 90°C, 60 min).

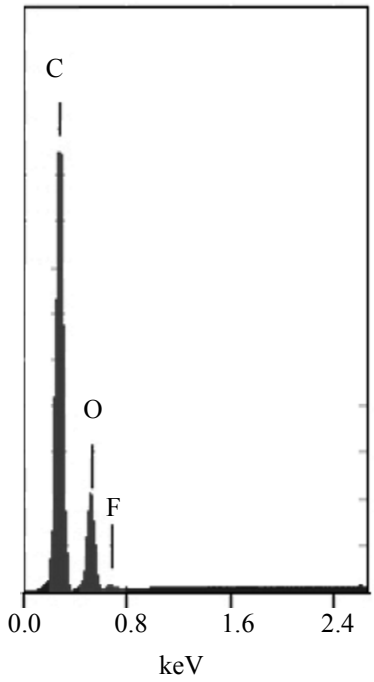

Fig. 2. EDX spectrum of the polyester fabric treated with a Forum solution in supercritical carbon dioxide (20 MPa, 90°C)

conditions indicated contains ca. 0.5 wt % fluorine [10, 12]. Based on the atomic-force microscopic data [11, 12], the average thickness of the resulting coating was estimated at 20 nm. Thermal analysis showed that thermal degradation of the fibrous material is unaffected by the nanosized fluoropolymer film occurring on the fabric surface [12].

Table 1 lists the indicators of hydrophobicity of the fabric treated at different parameters and, for comparison, those for the polyester fabric surface-treated with Nuva TTH (Clariant, Switzerland) which is one of the most effective commercial fluorine-containing hydrophobizing agents [25]. We did not estimate the contact angle for the untreated fabric, because the water droplet applied to its surface was instantly absorbed. Along with the contact angle, we determined the percentage of water absorption by the fabric (the amount of water retained during 1 h by the

Table 1. Contact angles of the polyester fabric treated with a Forum solution in supercritical carbon dioxide

Forum treatment conditions	Forum content per unit surface area of the fabric, g m^{-2}	Contact angle, deg	Percentage of water absorption
No treatment	not determined	not determined	38.0±0.3
20 MPa. 90°C	0.75±0.01	137±3	3.7±0.1
40 MPa. 70°C	0.50±0.01	139±3	5.5±0.1
50 MPa. 70°C	0.93±0.01	138±3	4.0±0.1
50 MPa. 90°C	0.86±0.01	135±3	4.0±0.1
Treatment with an aqueous dispersion of Nuva TTH (30 g l^{-1})	1.59±0.01	132±4	12.0±0.2

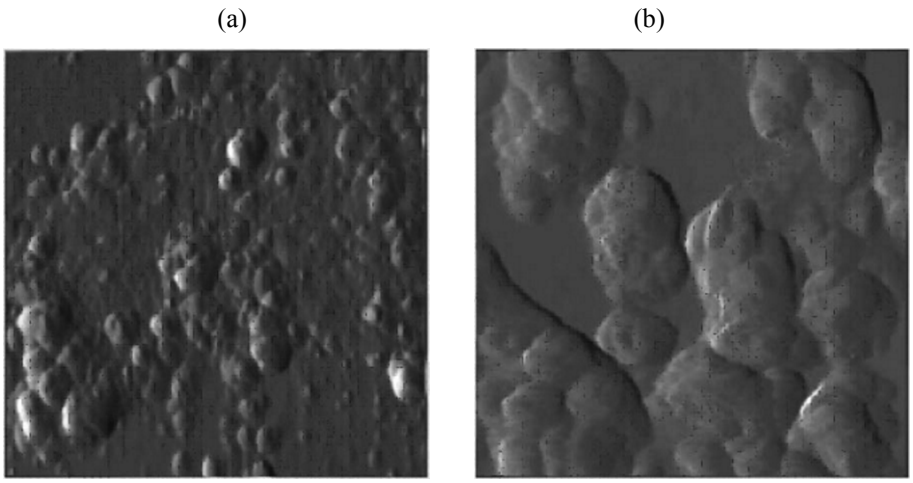

Fig. 3. The AFM images of the surface of the polyester film treated with a Forum solution in supercritical carbon dioxide (20 MPa, 90°C) with additions of cosolvents: (a) 5% methanol (5×5 μm section); dimensions of the formations: height 50 nm, area 0.2×0.2 μm and (b) 5% butanol (5×5 μm section); dimensions of the formations: height 350 nm, area 1×2 μm.

sample totally immersed into water), as prescribed by GOST (State Standard) 3816-81 ISO 811-81.

The tabulated data show that the contact angles of the polyester fabric treated by the new procedure slightly exceed those characterizing the ultrahydrophobicity of the fabric treated with a Nuva dispersion, while the weight of the fluoropolymer coating in the former case is much smaller. The percentage of water absorption by the fabric with the fluoropolymer coating deposited from supercritical carbon dioxide is uniquely low. A possible reason is that, owing to high wetting power of supercritical CO_2 toward hydrophobic surfaces and ability to penetrate into the inter-fiber space of the fabric, the entire surface of the fabric fiber is coated.

The fabric hydrophobized with Forum exhibit improved performance characteristics (Table 2). The treated polyester fabric acquires ultrahydrophobicity and a record-low percentage of water absorption. The water vapor permeability of the fabric increases, while its air permeability slightly decreases.

Much different results were obtained for the polyester film which is similar in the chemical composition to the fiber though has a continuous, smooth surface. Comparison of the hydrophobicity indicators of the treated polyester fabric and film shows that the contact angle of the hydrophobized fabric significantly exceeds that of the film (137° against 119°). The reason is that, unlike a flat smooth film, the fabric is constituted by interwoven, twisted multifilament threads and is characterized by the presence of macro- and microroughness. According to modern views, the wetting and water-repelling properties are significantly affected by the wetted surface curvature [26]. Also, the wetting regime for solids is strongly dependent on the roughness level [5, 27]: A rough nanostructured surface is characterized by a heterogeneous wetting regime in which the highest contact angles are achieved. It is believed that natural nanostructured surfaces exhibit superhydrophobicity (the so-called lotus effect) owing specifically to the heterogeneous wetting regime [28]. The uniformity of the fluoropolymer coating over the

Table 2. Consumer properties of the polyester fabric hydrophobized with a Forum solution in supercritical carbon dioxide

Characteristic	Fabric treated at 20 MPa, 90°C	Untreated fabric
Contact angle, deg	137±3	–
Percentage of water absorption	3.7±0.1	38±0.3
Air permeability, $dm^3\ m^{-2}\ s^{-1}$	125±15	160±24
Water vapor permeability, mg $cm^{-2}\ h^{-1}$	4.45±0.15	4.00±0.18

Table 3. Characteristics of hydrophobicity of the polyester fabric treated with a Forum solution in supercritical carbon dioxide (20 MPa, 90°C) with additions of cosolvents (5 and 10%)

Cosolvent	Contact angle, deg		Percentage of water absorption, %	
	5%	10%	5%	10%
No cosolvent	137±3		3.7±0.1	
Methanol	119±3	140±3	16.6±0.1	3.6±0.1
Ethanol	121±3	139±3	15.7±0.1	5.1±0.1
Butanol	118±3	139±3	14.4±0.1	7.2±0.1
Isobutanol	119±3	132±3	15.8±0.1	8.2±0.1

polyester film and the fabric was confirmed by the scanning electron microscopic, elemental, and EDX analysis data [10–12]. The surface fluoropolymer film replicates the microrelief features of the substrate, smooth for the polyester film and rough for fabric, for which reason the surface structure of the polyester sample is responsible for the wettability difference between the film and the fabric.

The above-said suggests the possibility of controlling the hydrophobic properties of fabrics by varying the composition and morphology of the fluoropolymer coating. To test this possibility, we attempted expanding the range of properties of the supercritical solvent, whose molecules are characterized by zero dipole moment, via introduction of polar compounds therein. To this end, we used 5 and 10 wt % additions of aliphatic alcohol as cosolvents.

An atomic-force microscopic examination of the polyester film with fluorine-containing coatings deposited from supercritical carbon dioxide added with cosolvents revealed the emergence on the fluoropolymer coating of formations responsible for increased roughness of the polyester film. Specifically, the AFM images show that the quantitative and qualitative characteristics of roughness depend on the cosolvent type and concentration (Fig. 3).

Table 3 presents the data which can be used for analyzing how the cosolvent type affects the contact angles and water absorption of the polyester fabric. The introduction of cosolvent leads predominantly to lower contact angles of the polyester fabric. The cosolvents are apparently adsorbed on the surface of polyester substrate, thereby preventing the formation of a chemically uniform ordered fluoropolymer film and leading to a thicker and less ordered coating for which the beneficial effect of roughness does not compensate for the increase in thickness.

The above-mentioned structural formations tend to increase in size with the cosolvent content increasing from 5 to 10%. The atomic-force microscopic examination showed that, with methanol as cosolvent, the height of the formations increases from 50 to 70 nm on the average, and their area, from 0.2×0.2 to 0.5×0.5 μm^2. With butanol, the height remains unchanged (350 nm), and the area increases from 1×2 to 1.5×4.5 μm^2. As the cosolvent content increases, the adverse effect exerted by increasing thickness and degree of disorder in the film on the hydrophobicity tends to diminish because of the growing microroughness of the coating, and with 10% alcohol the degree of hydrophobicity of the fabric even exhibits a growing trend.

Considering an important role played by the surface micro- and nanoroughness in hydrophobization of articles [5, 28–31], a chemical activation procedure was developed for polyester (polyethylene terephthalate) fibrous material [32] with a view to achieve stronger attachment of textile functional agents to the fabric surface. This procedure is based on weakly alkaline hydrolysis of the surface-localized macromolecules of the fiber-forming polymer at the ester bonds of polyethylene terephthalate, giving rise to active oxygen-containing groups. The choice of the process parameters and catalyst was dictated by the need to ensure formation of a maximum possible number of active groups on the surface of the material, provided that its strength characteristics will be preserved to a maximum possible extent. An additional implication of weak hydrolysis of polyethylene terephthalate consists in emergence of surface microroughness in the fibrous material. It was found that a urea solution is the most effective modifying agent.

The degree of surface modification of the polyethylene terephthalate material was estimated

Table 4. Indicators of stability of the hydrophobic effect under conditions of use of the polyester fabric

Fabric treatment agent	Initial contact angle, deg	Contact angle, deg, after		
		100 abrasion cycles	5 washing cycles	5 dry cleaning cycles
Solution of Forum in supercritical carbon dioxide (at 20 MPa, 90°C)	137±3	131±3	136±3	135±3
Aqueous dispersion of Nuva TTH (30 g l^{-1})	132±4	117±4	108±5	126±5

from the atomic-force microscopic data which indicated the formation on the film surface of hollows measuring 3–5 nm in depth and ~300 nm in length.

Treatment of the fabric, modified by the above-described procedure, with a Forum solution in supercritical carbon dioxide gave a material characterized by the hydrophobicity degree corresponding to the contact angle of 142° against 137° for the unmodified fabric. The stability of the hydrophobic effect was assessed from the contact angle of the treated fabric subjected to a number of tests (Table 4). The tabulated data show that the indicator of hydrophobicity of the fabric treated by the new procedure remains virtually unchanged under conditions of use, by contrast to the treatment procedure with Nuva.

Thus, treatment of the polyester fabric with a solution of ultradispersed polytetrafluoroethylene in supercritical carbon dioxide results in formation on the surface of the fibers constituting the fabric of an ultrathin low surface energy coating possessing an ordered structure and demonstrating high stability under conditions of use. The modification process can be implemented as a closed cycle in an environment-friendly manner with negligible waste generation. This factor further validates the technologies based on the use of supercritical carbon dioxide as a promising option for textile industry. It should be noted that a number of such technologies have been successfully implemented in the textile sectors of Germany and Japan, in dyeing processes for the most part [33, 34].

Coating Deposition from Acetone Solution of Tetrafluoroethylene Telomers

Another promising approach to surface modification of polyester fabrics is based on the use of an acetone solution of tetrafluoroethylene telomers (Cherflon trademark). This agent was developed at the Institute of Problems of Chemical Physics, Russian Academy of Sciences, with the use of radiation-chemical initiation (^{60}Co γ-rays) of tetrafluoroethylene telomerization in acetone [35].

It will be recalled that telomerization is a special type of polymerization carried out in the presence of telogens, efficient chain transfer agents. Telomerization gives a mixture of low-molecular-weight homologous compounds (telomers) characterized by the degree of polymerization ≤ 5–20. With γ-irradiation initiation, there is no need in introduction of reaction initiators and telogens into the telomerization system: The reaction is initiated by the radicals formed from the solvent molecules under the action of radiation, and the solvent molecules can act as chain-transfer agents.

With acetone as solvent, formation of tetrafluoroethyelene telomers follows the scheme:

(1) chain initiation by the radicals (R) formed from solvent radiolysis ($\dot{H}$, $\dot{C}H_3$, $\dot{C}H_2COCH_3$);

(2) chain propagation $\dot{R} + C_2F_4 \rightarrow \dot{R}–CF_2–CF_2$;

(3) chain transfer via solvent $\dot{R}–(C_2F_4)_n + CH_3COCH_3 \rightarrow R–(C_2F_4)_nH + \dot{C}H_2COCH_3$;

(the CH_2COCH_3 radical generated thereby initiates a new telomerization chain); and

(4) chain termination by recombination of $\dot{R}–CF_2–CF_2$, $\dot{C}H_3$, $\dot{C}H_2COCH_3$ radicals.

This scheme gives a mixture of low-molecular-weight homologous compounds $R^1(C_2F_4)_n–R^2$, where R^1 and R^2 = H, CH_3 or $COCH_3$ and CH_2COCH_3. The coefficient n varies within 3–20 depending on the reaction conditions (initial monomer concentration in the solvent) [36].

The radiation-initiated telomerization of tetrafluoroethylene can be run in the presence of other solvents as well. For example, with butyl chloride the main product of tetrafluoroethyelene telomerization will be $C_4H_8Cl(C_2F_4)_{n–1}CF_2CF_2H$, and also small amounts of $C_4H_9(C_2F_4)_{n–1}CF_2CF_2H$ and $Cl(C_2F_4)_{n–1}CF_2CF_2H$ will be formed [37]. The average number of units in the telomer n increases from 7 to 16 as the monomer concentration in solution increases from 7 to 22 wt %.

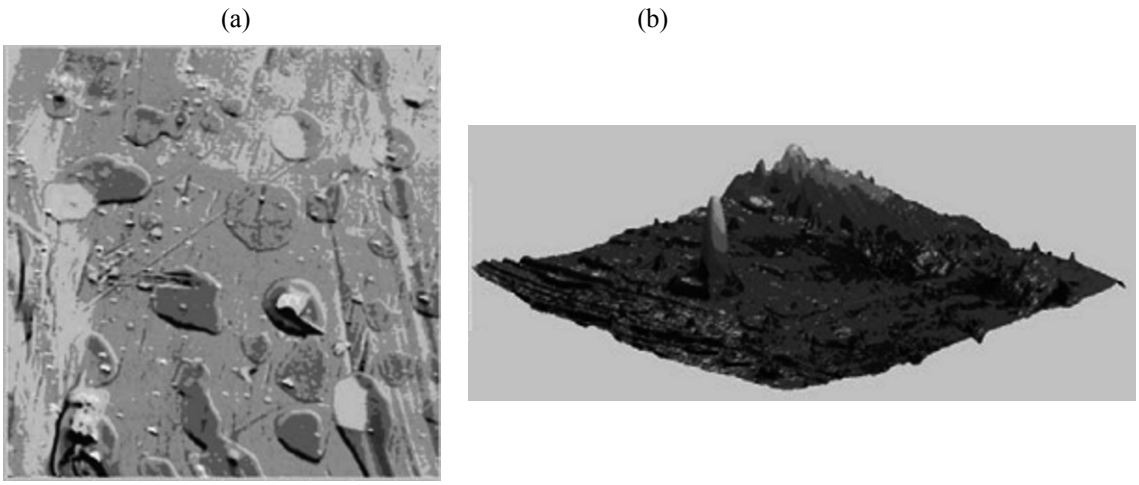

Fig. 4. The AFM mages of the surface of the polyester fabric with a coating formed from tetrafluoroethylene telomers: (a) phase image and (b) image in 3D representation. Dimensions of the formations: diameter of "islands" 0.75–1.5 μm, height 4–9 nm, height of conical formations 10–20 nm.

The morphological structure of the product yielded by deposition from an acetone solution of tetrafluoroethyelene telomers onto a silicon substrate was examined earlier [38, 39]. At the supramolecular level, this product is distinguished from polytetrafluoroethyelene by a more disordered structure whose degree of disorder decreases upon subsequent heat treatment. The resulting 1–5-μm-thick fluoropolymer film imparts new surface properties to the material.

The Cherflon agent was deposited onto the polyester material with the use of a spraying device; the amount of the telomer deposited was changed by varying the number of treatment cycles. Considering the fact that the resulting coating has an "island" rather than a continuous nature [37], the coating was heat-treated at 180–200°C for 10 min to achieve the continuity. Heating causes softening of the fluoropolymer and its spreading over the substrate surface, thereby leading to a continuous fluoropolymer film. The same result was achieved on the fabric surface by ironing after the telomer deposition and air drying stages [12, 14].

The presence of a fluoropolymer coating was confirmed by the results of an IR-spectroscopic (MATR) examination: The spectra contain bands near 1150 and 1210 cm^{-1}, characteristic for fluoropolymers. An insight into the morphology of the resulting coating was provided by the AFM images (Fig. 4).

The fluoropolymer coating surface shows a markedly uneven surface with traces of "island" formations. The unevenness of the film surface is also evidenced by scatter of the EDX and elemental data analysis data. The thermogravimetric and differential thermal analysis data for the initial fabric and that treated with tetrafluoroethylene telomers are virtually identical. They suggest that the formation of a fluorine-containing film on the fabric surface does not affect thermal degradation of the fibrous material [12], evidently due to a small amount of the telomers deposited onto the fabric. The differential thermal analysis data showed that the heat treatment caused the content of the low-molecular-weight fraction of the fluoropolymer on the fabric to decrease [12].

To obtain coatings with a more ordered structure, the telomer-treated samples were subjected to complex deformation under the influence of a stress (abrading test). Specifically, as a vertical normal load (440 g cm^{-3}) was applied to the sample, shear stress was gradually applied horizontally. As a result, weakly attached excessive telomers were removed from the fabric surface.

Table 5 shows that deposition of the tetrafluoroethylene telomers onto the polyester film surface causes the contact angle to increase by 20°. For the fabric subjected to abrading effect the contact angle slightly decreases, and the microrelief of the telomer

Table 5. Hydrophobicity of the polyester film with a tetrafluoroethylene telomer layer deposited in three cycles

Type of treatment	Contact angle, deg
No treatment	72±3
Telomer deposition	92±3
Telomer deposition and abrasion	88±2

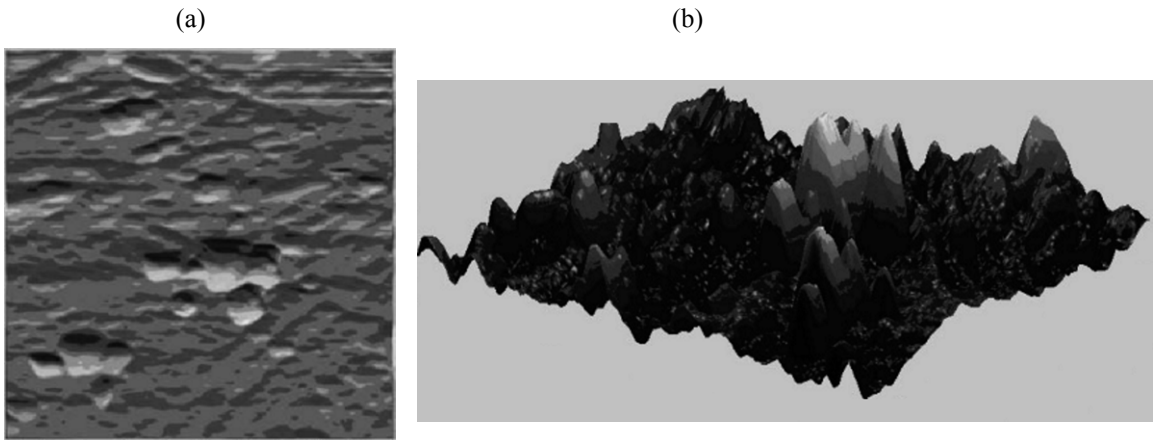

Fig. 5. The AFM image of the surface of the polyester film with a telomer coating (three deposition cycles) after abrasion: (a) phase image and (b) image in 3D representation. Average roughness 20 nm.

film is characterized by nanoroughness (see Fig. 5). At the same time, the abrasive forces destroy larger formations, traces of "island" coating. This causes a decrease in the degree of surface microroughness and, thereby, a certain decrease in the contact angle.

The real object of hydrophobization in textile industry is a fabric, rather than a film, from which it significantly differs in structure and properties. Table 6 lists the contact angles of the fabric subjected to different numbers of cycles of treatment with tetrafluoroethylene telomers and to abrading effect. It is seen that the polyester fabric coated with a telomer film acquires better water-repelling properties, close to those achieved through the use of highly effective concentrated Nuva TTH agent. The contact angle for the polyester fabric exceeds by 35° that for the polyester film treated under identical conditions. This is apparently associated with a complex morphological structure of the fabric which is constituted by interwoven cylindrical threads and is characterized by the presence of macro- and microroughness. Our data correlate well with the results of the theoretical and experimental studies demonstrating how the hydrophobicity is influenced by the wetted surface curvature and roughness [5, 26–29].

The effect of abrasive forces on the fabric subjected to one or two cycles of treatment with the telomers causes additional, very substantial, increase in the contact angle (by 10°–16°). Abrasion removes the excessive amount of telomers from the fabric, whereby the coating gets very thin and acquires nanoroughness. Presumably, the additional increase in the contact angle is due to the combined effect exerted on wetting by the macro- and microroughness of the fabric surface

Table 6. Hydrophobicity of the polyester fabric treated with tetrafluoroethylene telomer solutions

Type of treatment	Contact angle, deg	
	before abrasion	after abrasion
No treatment	Not determined	Not determined
Number of treatment cycles		
one	127±5	143±5
two	127±5	137±5
three	129±5	129±5
Treatment with an aqueous dispersion of Nuva TTH (30 g l^{-1})	132±4	129±4

Table 7. Hydrophobicity of the polyester fabric subjected to chemical activation and treated with a tetrafluoroethylene telomer solution

Type of treatment	Contact angle, deg	
	before abrasion	after abrasion
One treatment cycle	127±5	143±5
Activation, one treatment cycle	131±5	139±5
Two treatment cycles	127±5	137±5
Activation, two treatment cycles	135±4	146±4
Three treatment cycles	129±4	131±4
Activation, three treatment cycles	130±3	137±3

Table 8. Comparative stability of the hydrophobic effect under conditions of use of the polyester fabric subjected to activation and treated with a tetrafluoroethylene telomer solution

Treatment type	Initial	Contact angle, deg, after		
	contact angle, deg	100 abrasion cycles	5 washing cycles	5 dry cleaning cycles
Activation, three Cherflon treatment cycles	130±3	135±3	134±3	130±3
Treatment with an aqueous dispersion of Nuva TTH (30 g l^{-1})	132±4	117±4	108±5	126±5

relief pattern, which is replicated by the hydrophobizer film because of its small thickness and the intrinsic nanoroughness of the telomer coating. The abrading effect also causes a decrease in the percentage of water absorption by the fabric, which fact is due, in our opinion, to ordering of the structure of the protective coating and elimination of its microdefects.

Activation of the surface of the polyester fabric fibers, responsible for additional amount of active groups and larger nanoroughness of surface [32], causes enhancement of hydrophobicity of the polyester fabric (Table 7). Treatment of the activated polyester fabric with acetone solutions of tetrafluoroethylene telomers causes the contact angle to increase by 1°–8°. Upon exposure to abrading effect the contact angle further increases by 7°–11°. Evidently, chemical activation causes formation of a more ordered continuous less defective protective film on the fabric surface. The same co conclusion follows from a decrease in the percentage of water absorption by the fabric from 18 to 15 (against 38 for the untreated fabric).

The stability of the hydrophobic effect was assessed by measuring the contact angle of the fabric exposed to medium-severity conditions of use: 100 abrasion cycles, 5 washing cycles, and 5 dry cleaning cycles. Table 8 lists the hydrophobicity characteristics of the polyester fabric after preliminary activation and three cycles of treatment with a tetrafluoroethylene telomer solution (Cherflon agent), as well as of that treated with Nuva TTH. By contrast to the treatment procedure with Nuva TTH, the deposition of the telomer coating onto the polyester fiber surface resulted in a degree of hydrophobicity that does not decrease upon exposures to medium-severity conditions of use, which seem to beneficially affect the coating structure.

High air permeability of the fabric is preserved (111 dm^3 m^{-2} s^{-1}, ~70% of the initial level), and the water vapor permeability remains unchanged, 4.00 mg cm^{-2} h^{-1}.

Our results suggest that the use of acetone solutions of tetrafluoroethyelene telomers allows deposition onto the fabric fiber surface of a coating which, after a heat treatment, will form a thin fluoropolymer film that will imparts ultrahydrophobicity to polyester fabrics, while maintaining high air and water vapor permeability levels. The hydrophobicity of the polyester fabric can be additionally increased by controlling the coating thickness and ordering (abrading effect), as well as by affecting the microrelief features of the fabric (preliminary chemical activation of polyester material). The structure ordering effect is also achieved for the coating exposed to medium-severity conditions of use.

A negative aspect hindering the use of these results for development of an effective technology of hydrophobization of polyester fibrous materials consists in the use of acetone. In this connection, studies dedicated to synthesis of other solvents able to dissolve tetrafluoroethylene are currently under way at the Institute of Problems of Chemical Physics, Russian Academy of Science, and Krestov Institute of Solution Chemistry, Russian Academy of Sciences, with a view to application of these solvents as hydrophobizing agents [39, 40]. Also, telomers proved to be soluble in supercritical carbon dioxide, and the use of this solvent may provide a promising option for fabric modification.

CONCLUSIONS

We demonstrated the possibility and effectiveness of modification of polyester fibrous materials via formation on the surface of their constituting fibers of a nanosized coating based on low-molecular-weight polytetrafluoroethylene. The coating imparts to the fibrous material a high hydrophobicity intrinsic to the fluoropolymer. The surface fluoropolymer film replicates the rough microrelief surface pattern of the fibrous material. Preliminary chemical modification of the fibrous material, resulting in increased roughness, can also contribute to enhanced hydrophobicity. Small

(nanoscale) thickness of the coating is responsible for its high stability under conditions of use.

ACKNOWLEDGMENTS

This study was financially supported by the Russian Foundation for Basic Research (project nos. 08-03-12152-ofi and 11-03-12048-ofi-m-2011), Division of Materials Science and Chemistry, Russian Academy of Sciences (Program no. 7 "Development of Scientific Principles of Environment-Friendly Resource-Saving Chemicotechnological Processes: Optimization of Processes with Production of Experimental Batches of Substances and Materials" for 2009, 2010, and 2011).

The authors are grateful to the colleagues who participated in carrying out the research work: A.V. Khorev (Institute of Solution Chemistry, Russian Academy of Sciences), A.E. Zavadski and I.V. Kholodkov (Ivanovo State University of Chemical Technology), A.G. Buyanovskaya, Yu.E. Vopilov, N.M. Kabaeva, L.V. Gumileva, I.G. Barakovskaya, and R.U. Takazova (Institute of Organoelement Compounds, Russian Academy of Sciences), G.Yu. Yurkov (Baikov Institute of Metallurgy and Materials Science, Russian Academy of Sciences), and A.I. Bol'shakov and G.A. Kichigina (Institute of Problems of Chemical Physics, Russian Academy of Sciences).

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