ISSN 1070-4272, Russian Journal of Applied Chemistry, 2009, Vol. 82, No. 4, pp. 622−629. © Pleiades Publishing, Ltd., 2009.
Original Russian Text © A.K. D'yakova, S.A. Trifonov, E.A. Sosnov, A.A. Malygin, 2009, published in Zhurnal Prikladnoi Khimii, 2009, Vol. 82, No. 4, pp. 628−634.

MACROMOLECULAR CHEMISTRY AND POLYMERIC MATERIALS

Effect of Chemical Modification on Structural and Energy Characteristics of the Surface of Polyethylene and Polyvinyl Chloride Films

A. K. D'yakova, S. A. Trifonov, E. A. Sosnov, and A. A. Malygin

St. Petersburg State Institute of Technology (Technical University), St. Petersburg, Russia

Received December 30, 2008

Abstract—The possibility of controlling the surface energy and wettability of polyvinyl chloride and polyethylene films by chemical gas-phase modification was studied. The surface of the initial and chemically modified polymeric materials was examined by atomic force microscopy.

DOI: 10.1134/S107042720904017X

Polyethylene and polyvinyl chloride (PVC) are among the most widely used polymers today, owing to good dielectric characteristics, high chemical resistance, and strength. These materials are vinyl polymers with the repeating unit $[–CH_2–CH_2–]_n$, with one of the hydrogen atoms in PVC substituted by the chlorine atoms. However, in many cases the use of these materials is considerably restricted because of their low surface energy, which leads to poor adhesion and low wettability of the surface. These properties largely depend on the chemical composition and structure of the surface layer and can be controlled by two main methods: removal of weak boundary layers of the polymer and formation of new active centers altering the surface energy [1, 2].

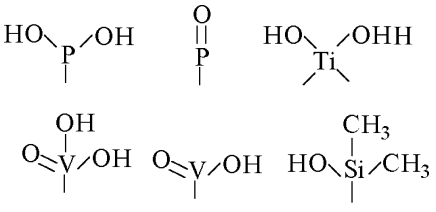
One of the methods for forming new functional structures on the surface of polymeric materials is gas-phase modification of matrices using principles of molecular layering (ML) [3]. This method consists in performing chemical reactions between externally supplied reagents and the functional groups of the support under essentially nonequilibrium conditions. The ML technique proved to be very efficient for controlling the macroscopic properties of phenol–formaldehyde, polyamide, epoxy, and other polymeric materials. According to the results of IR studies, chemical modification involves grafting of element-containing structures to surface reaction centers of polymers (double bonds, oxygen-containing groups, hydrogen at tertiary carbon atom), which leads to changes in the thermal oxidation, electret, diffusion, and other properties of materials [4–7].

In this study we examined how the chemical composition of polyvinyl chloride and low-density polyethylene (LDPE) films modified with vapors of volatile halides [PCl_3, $TiCl_4$, $VOCl_3$, and $Si(CH_3)_2Cl_2$] affects the energy characteristics, wettability, and topography of the polymer surface.

EXPERIMENTAL

The effect of chemical modification was studied with films of low-density polyethylene of 158-03-020 grade and Pentaprint polyvinyl chloride. The functional use of these materials is largely determined by the energy characteristics, including the wettability of the surface. As modifying agents we chose low-boiling halides of phosphorus, vanadium, titanium, and silicon.

The sample modification was performed in a flow-type reactor under the conditions described in [4, 6]. According to the results of chemical analysis, the content of modifying elements in the polymer films is about 10^{-3} mmol cm^{-2} [8, 9]. Presumably, chemical modification of the polymeric materials results in formation in their surface layer of element–hydroxyl, element–oxygen, and element–methyl groups:



The energy characteristics of the surface of the materials were determined by measuring the contact angles of the initial and modified films with test liquids (water and glycerol) in the advancing mode. The liquid drop volume was about 10 μl. The equilibrium contact angle θ was determined from the kinetic curves of wetting and spreading of a liquid drop, from a portion of a plateau where the parameter had a constant value for a definite period. In the calculations we used the statistical average value of the contact angle, obtained from ten measurements. The measurement error did not exceed 3%. The surface energy γ_s and its polar (γ_s^p) and dispersive (γ_s^d) components were calculated by the Fowkes method [10, 11] using two wetting liquids:

$$\begin{cases} \gamma_{l1} = \dfrac{(1+\cos\theta_{11})}{2} = \sqrt{\gamma_{11}^d \gamma_s^d} + \sqrt{\gamma_{11}^p \gamma_s^p}, \\ \gamma_{l2} = \dfrac{(1+\cos\theta_{11})}{2} = \sqrt{\gamma_{12}^d \gamma_s^d} + \sqrt{\gamma_{12}^p \gamma_s^p}, \end{cases}$$

where θ_{li} is the advancing contact angle, and γ_{li}, γ_{li}^d, and γ_{li}^p, surface energy and its dispersive and polar components for *i*th test liquid.

The morphology of the surface of polymer films was studied by atomic-force microscopy (AFM) on a Solver P47 Pro scanning probe microscope (NT-MDT, Russia) in the tapping mode. The samples were scanned in two modes: topographic surveying and phase contrast, to obtain information on the relief and surface properties of the materials. In the phase contrast mode, analysis of changes in the phase shift Δφ of the amplitude–frequency characteristic of the cantilever, caused by adhesion interactions, makes it possible to reveal changes in the composition of particular areas of the sample surface [12].

Contact angles θ for PVC and LDPE films

Modifying element	θ, deg			
	PVC		LDPE	
	water	glycerol	water	glycerol
—	88	72	98	82
Phosphorus	36	43	66	73
Vanadium	64	68	56	65
Silicon	96	85	113	99
Titanium	94	83	93	83

The contact angles of the initial and modified samples with water and glycerol are given in the table.

As can be seen, the surface of the initial PVC samples becomes more polar as compared to LDPE. Lower contact angles of polyvinyl chloride are apparently associated with the presence of chlorine-containing groups in the polymer macromolecules. Treatment of the films with phosphorus chloride and vanadium oxychloride vapors makes the surface more hydrophilic. After modification of the polymer matrices with dimethyldichlorosilane, their surface becomes more hydrophobic. It should be noted that, after treatment of PVC and LDPE films with $TiCl_4$ vapor, the contact angles of these materials become equal (see table). According to AFM data given in [7], synthesis of titanium oxide structures on the surface of a composite material based on polyethylene leads to the formation of a uniform coating. Similar changes in the surface topography of modified films apparently favor leveling of the energy state of the polymer matrices.

From the measured contact angles, we calculated the surface energy and its components for the initial and modified samples. The results are given in Figs. 1 and 2.

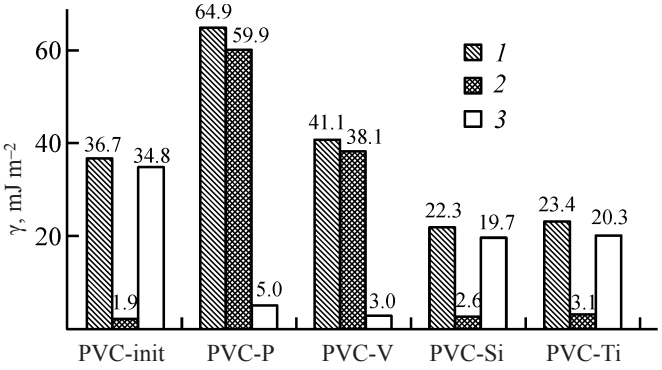


Fig. 1. Surface energy γ of the initial and modified PVC films. (*1*) Total surface energy, (*2*) polar component, and (*3*) dispersive component; the same for Fig. 2.

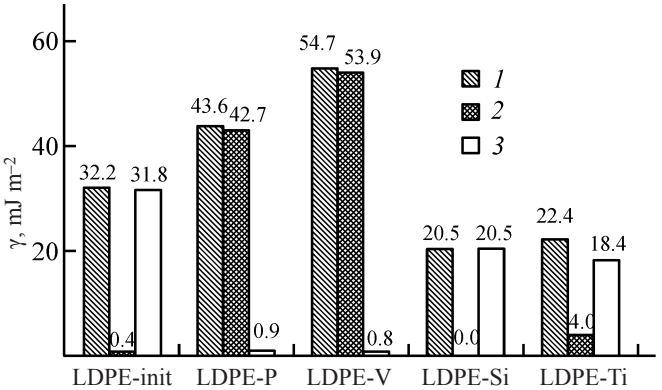


Fig. 2. Surface energy γ of the initial and modified LDPE films.

As follows from Figs. 1 and 2, the surface of the initial polymers is nonpolar. The major contribution to the surface energy (95% for PVC and 99% for LDPE) is made by the dispersive component (van der Waals interactions). The presence of an insignificant polar component may be due to the presence in polymers of defective structures. For example, the content of double bonds in LDPE is 0.3–0.5 per 1000 carbon atoms [13], and in PVC, 0.4–6 per 1000 monomeric units [14]. In addition, in polymer macromolecules there are oxygen-containing groups of various types. Their concentration is 0.01–0.1 and 0.5–1 group per 1000 monomeric units for LDPE and PVC, respectively [13, 14]. Apparently, the higher surface energy of PVC films is due not only to the presence of

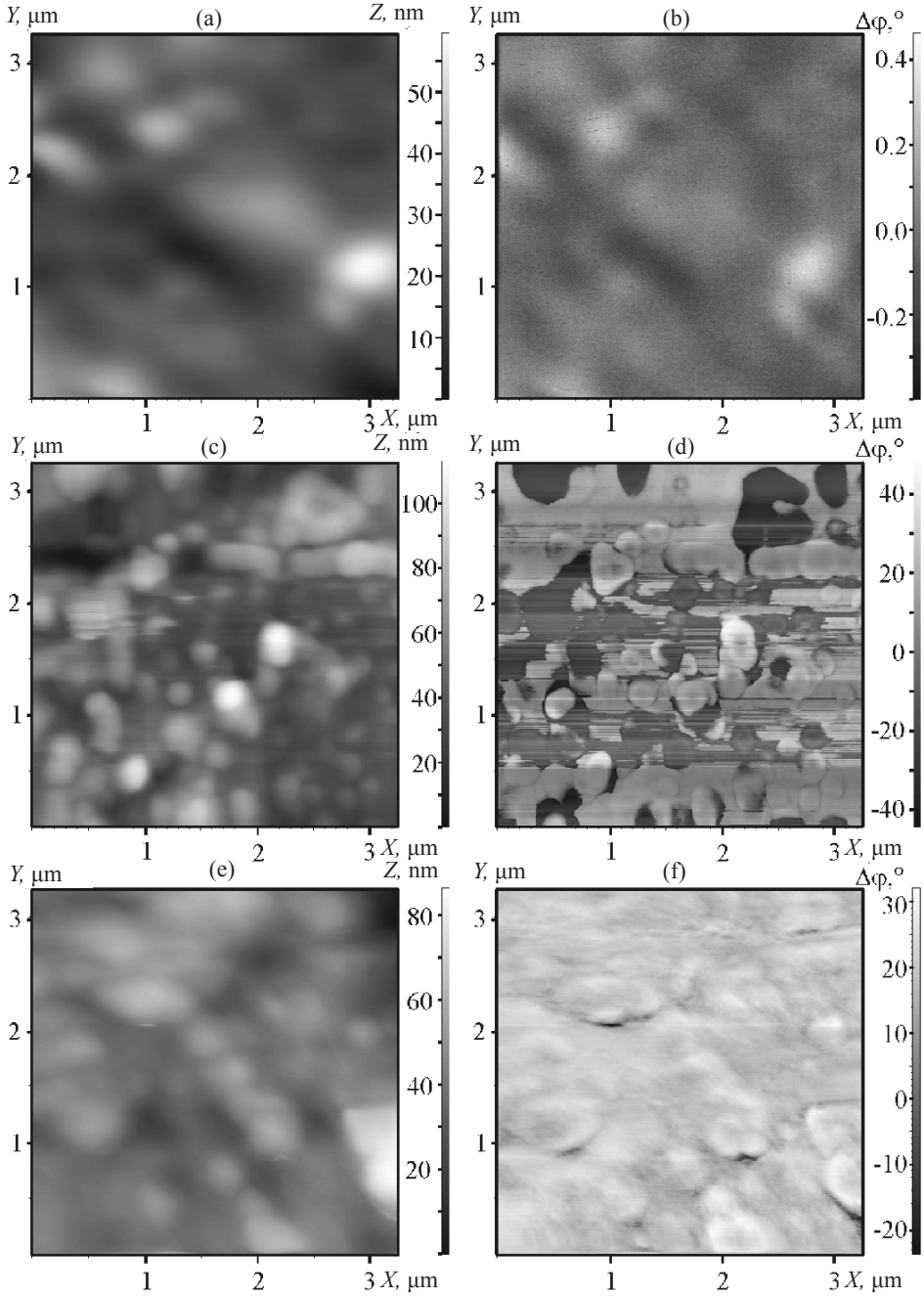


Fig. 3. AFM images of the surface of PVC film: (a, b) PVC-init, (c, d) PVC-P, (e, f) PVC-V, (g, h) PVC-Si, and (i, j) PVC-Ti. (a, c, e, g, i) Topographic image and (b, d, f, h, j) scanning in the phase contrast mode; the same for Fig. 4.

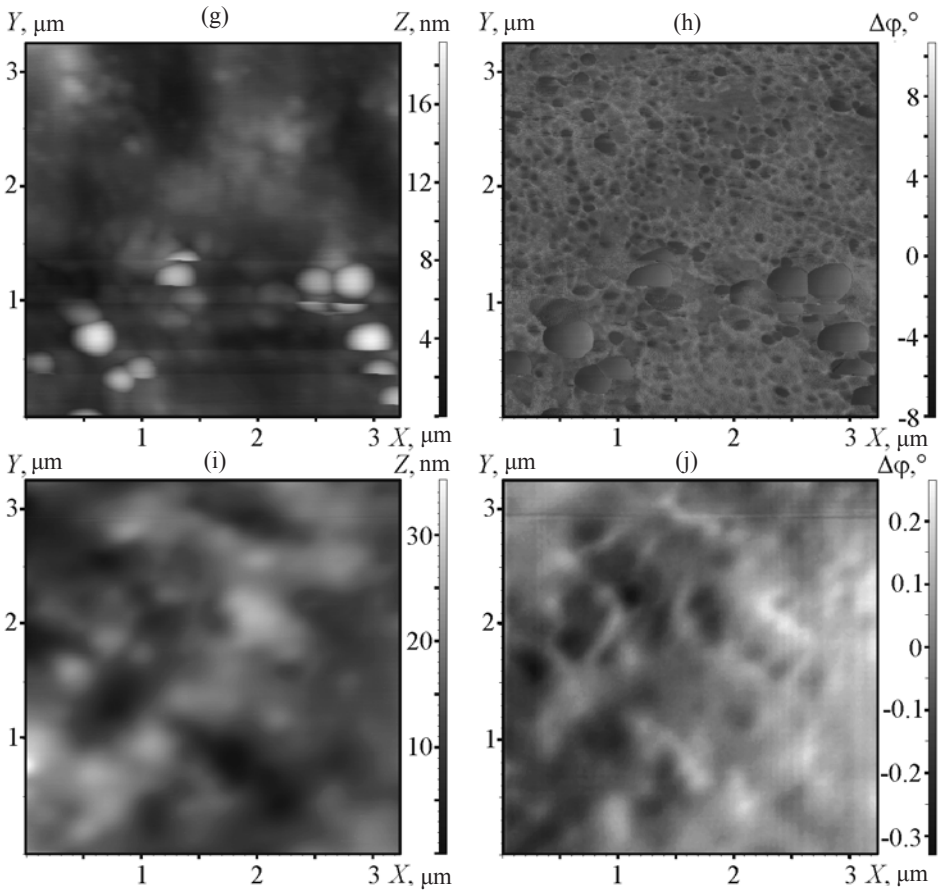


Fig. 3. (Contd.)

chlorine in the polymer chain but also to higher content of chemical defects in the polymer structure.

After treatment of the films with phosphorus oxychloride, the surface energy increases by a factor of 1.8 for PVC and 1.4 for LDPE, and the relative contributions of its components change (Figs. 1, 2). The major contribution to the total energy characteristic is made in this case by the polar component. It increases by a factor of more than 30 for polyvinyl chloride and by more than two orders of magnitude for polyethylene. The dispersive component of the surface energy decreases by a factor of approximately 7 and of more than 30 for PVC and LDPE, respectively. This change in the energy characteristics of the modified samples is apparently due to introduction into the surface layer of polar phosphorus- and oxygen-containing structures which actively interact with wetting liquids through both electrostatic forces and hydrogen and donor–acceptor bonding [5, 15, 16].

Similar trends in variation of the surface energy and its components are manifested for polymer samples modified with vanadium-containing structures. It should be noted, however, that, whereas with LDPE an increase in the energy parameter by a factor of ~1.7 is more significant compared to the treatment with phosphorus chloride, with PVC films the surface energy upon treatment with vanadium oxychloride increases relative to the initial film insignificantly, by only ~10% (Figs. 1, 2).

According to published data [5], chemical grafting of vanadium-containing structures is performed not only by exchange but also by redox reactions of $VOCl_3$ with reactive surface centers of the polymer matrix. Apparently, in contrast to PVC, treatment with vanadium oxychloride vapor of polyethylene films, which are oxidized more readily, leads to an increase in the concentration of oxygen-containing groups in the surface layer, which make an additional contribution to the polar component.

Gas-phase treatment of polyvinyl chloride and polyethylene films with dimethyldichlorosilane vapor leads to a decrease in the surface energy by 40% relative to the initial matrix. Introduction into the polymer surface layer of nonpolar dimethylsilicon fragments [$=Si(CH_3)_2$]

decreases the dispersive component by almost 30%. The polar component for both polymers varies insignificantly (Figs. 1, 2). Calculation of the surface energy for the polymers modified with titanium chloride vapor shows that this treatment also decreases the surface energy relative to the initial polymers. The major contribution (about 90 and 80% for PVC and LDPE, respectively) to the total surface energy is made by the dispersive component (Figs. 1, 2).

An AFM examination of the films showed that the surface of the initial polymers is covered by crystallites fused with each other, with the following characteristic sizes: lateral size 0.5–1.0 and 0.2–0.5 μm and height 10–20 and up to 40 nm for PVC and LDPE, respectively

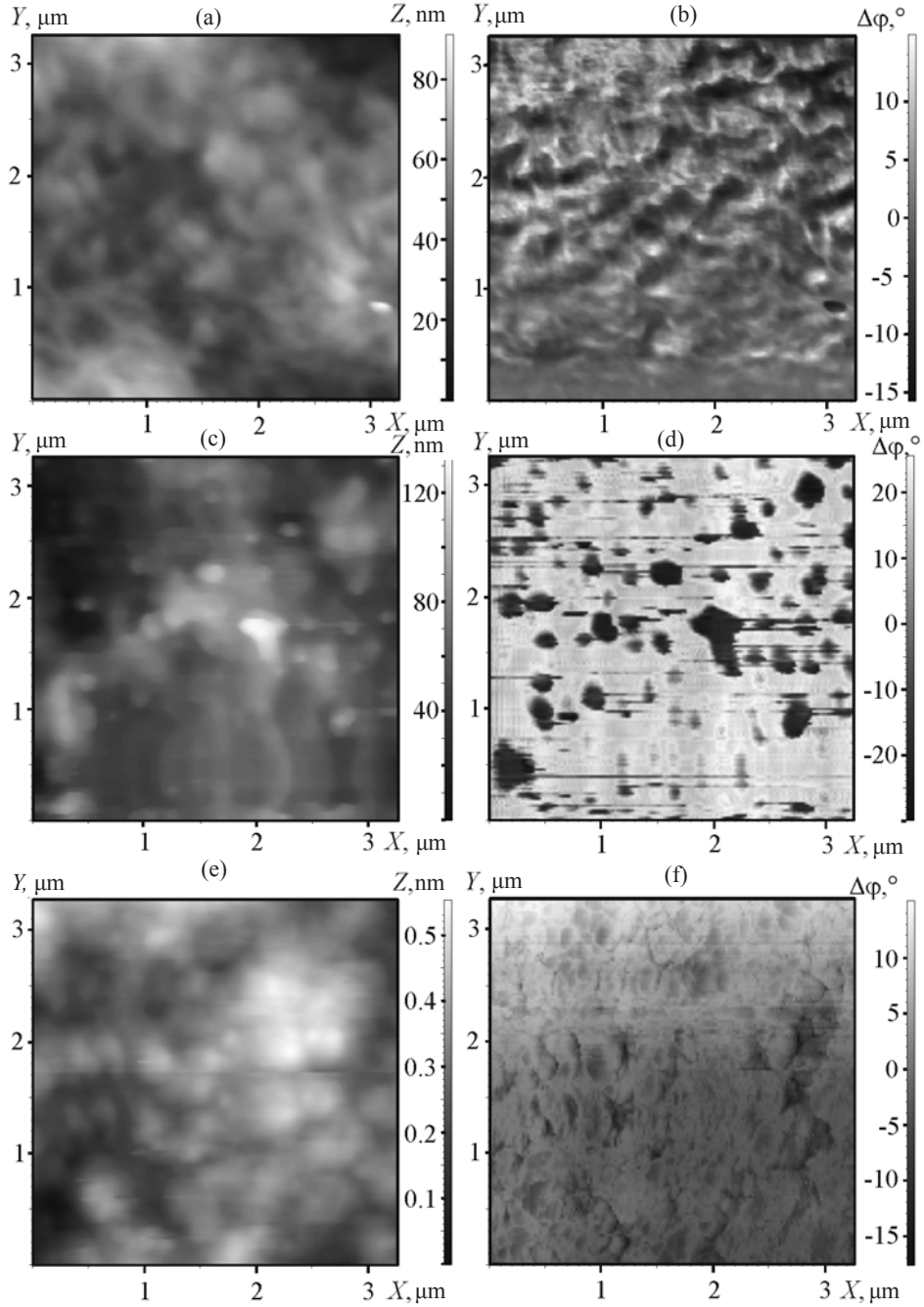


Fig. 4. AFM images of the surface of LDPE film: (a, b) LDPE-init, (c, d) LDPE-P, (e, f) LDPE-V, (g, h) LDPE-Si, and (i, j) LDPE-Ti.

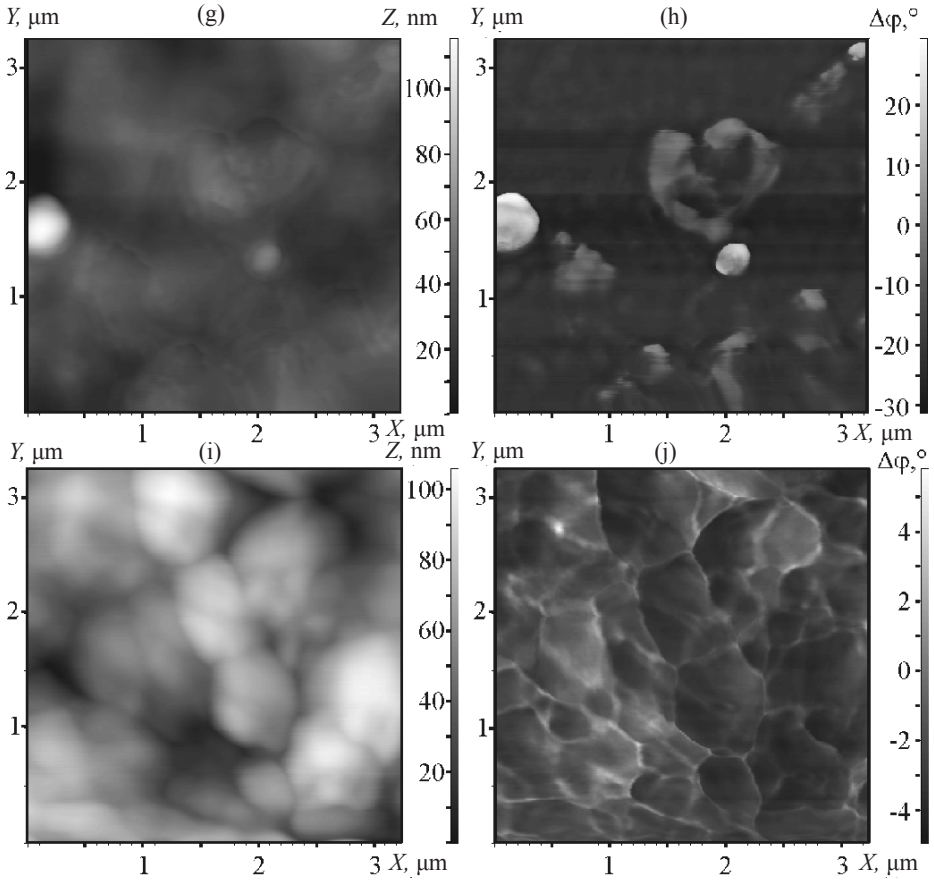


Fig. 4. (Contd.)

(Figs. 3a, 4a). Scanning of the surface in the phase contrast mode (Figs. 3b, 4b) revealed no regions with essentially different adhesion characteristics. The roughness of the surface layer of LDPE, determined on the 10×10 μm area in accordance with DIN 4768, is about 32 nm, which exceeds the corresponding value for the PVC film (~8 nm) and is due to the presence of topographic defects on the surface of the polyethylene matrix (Fig. 4b). The latter fact is apparently responsible for the increased phase shift Δφ, which is about 30° and 1° for LDPE and PVC, respectively.

Modification of the polymers with PCl_3 vapor alters the structure of the sample surfaces. In AFM images taken in the topographic mode (Figs. 3c, 4c), one can see separate areas with a lateral size of 200–300 nm, essentially differing in the adhesion characteristics (Δφ = 80° and 70° for PVC and LDPE, respectively) from the other surface. The boundaries of these areas cannot be clearly determined in the phase contrast mode, because cantilever movement is accompanied by partial transfer of the material from these areas to the adjacent areas of the matrix (Figs. 3d, 4d). This phenomenon may be caused by the fact that phosphorus oxide structures formed on the film surface in the course of chemical modification exhibit high hydrolytic activity [17], which leads to the formation of a hydration shell around the grafted groups owing to adsorption of water vapor from air. The roughness of the surface of the modified polymers varies insignificantly and is about 15 nm for PVC and 29 nm for LDPE.

According to published data [5], treatment of polyethylene with vanadium oxychloride vapor leads to partial oxidation of reactive centers of the polymer. The occurrence of these transformations on the polymer surface gives rise to intercrystallite boundaries and separate deep caverns with the lateral size of up to 200–250 nm in the sites of crystallite contact (Figs. 3e, 4e). Examination of modified samples in the phase contrast mode confirms changes in the chemical composition of the surface (Δφ ~40°–50°) and allows localization of areas of preferential addition of element-containing structures specifically in sites with the morphology distorted by redox reactions (Figs. 3f, 4f). Apparently, this effect increases the roughness of the surface of the vanadium-containing samples by a factor of 1.2–2.0 relative to the

initial films.

Treatment of the polymers with dimethyldichlorosilane vapor leads to the formation on the surface of silicon-containing structures with the lateral sizes of 0.3–0.5 (Fig. 3g) to 1.0 μm (Fig. 4g) for PVC and LDPE, respectively, and a height of up to 10 nm. Scanning in the phase contrast mode reveals clear boundaries of the synthesized structures (Figs. 3h, 4h). The adhesion characteristics of these formations differ insignificantly from those of the initial polymer surface, and the phase shift is about 6.5° (for PVC) and 30° (for LDPE).

As in the case of the samples modified with dimethyldichlorosilane, chemical grafting of titanium-containing groups smoothens the relief of the polymer films, with a decrease in the surface roughness to 3 and 29 nm for PVC and LDPE, respectively (Figs. 3i, 4i). Scanning in the phase contrast mode does not reveal significant differences in the adhesion characteristics of the surface, as indicated by a decrease in the phase shift by a factor of 2–3 relative to the initial polymers: to approximately 0.5° for PVC and 10° for LDPE (Figs. 3j, 4j). These changes may be due to uniform coating of the surface layer of the polymer matrices with titanium oxide groups, leading to equal contact angles of the polymer matrices (see table).

Thus, AFM examination of modified films revealed not only changes in the surface morphology of the initial and modified polymers but also a relationship between the chemical nature of the synthesized element-containing groups, the structure of the surface layer, and the energy characteristics of the products obtained. It should be noted that gas-phase treatment with volatile halides of various elements does not lead to essential changes of the surface topography of polymer films (except treatment with $VOCl_3$ vapor). Synthesis of vanadium- and phosphorus-containing structures on the surface increases the phase shift characterizing the adhesion properties of the surface layer by a factor of 1.3–1.8 for LDPE and 50–80 for PVC. These changes indicate that structures of a different chemical nature appear on the surface, leading to a considerable decrease in the contact angles of the modified samples (see table), an increase in the surface energy due to the polar component (Figs. 1, 2), and ultimately an increase in the hydrophilicity of the polymer films. Chemical grafting of silicon-containing structures, which are hydrophobic owing to the presence of methyl groups, decreases the phase shift by a factor of 2 and 3 for PVC and LDPE, respectively, relative to the initial matrices. The major contribution to a decrease in the surface energy of the modified samples is made by the dispersive component (Figs. 1, 2). According to the AFM data, the presence in the polymer surface layer of titanium-containing groups leads to formation of a uniform coating, which favors leveling of the energy state of the polymer matrices (see table).

CONCLUSIONS

(1) Modification of the surfaces of polyvinyl chloride and low-density polyethylene films with vanadium- and phosphorus-containing groups makes the surface layer of the polymers more hydrophilic, whereas silicon- and titanium-containing structures make it more hydrophobic.

(2) A relationship was revealed between the chemical nature of the additive, structure of the surface layer, and wettability of the modified polymers.

(3) Variation of the energy characteristics of the polymer surfaces mainly depends on the chemical nature of the forming element-containing groups.

ACKNOWLEDGMENTS

The study was financially supported in part by the Russian Foundation for Basic Research (project no. 07-03-00330) and program "Development of the Scientific Potential of Higher School) (project no. 2.1.1/2665).

REFERENCES

1. Povstugar, V.I., Kodolov, V.I., and Mikhailova, S.S., *Stroenie i svoistva poverkhnosti polimernykh materialov* (Structure and Properties of the Surface of Polymeric Materials), Moscow: Khimiya, 1988.
2. Potsius, A.V., *Klei, adgeziya, tekhnologiya skleivaniya* (Adhesives, Adhesion, Gluing Technology), St. Petersburg: Professiya, 2007.
3. Malygin, A.A., *Zh. Prikl. Khim*., 1996, vol. 69, no. 10, pp. 1585–1593.
4. Trifonov, S.A., Semenova, E.Yu., and Malygin, A.A., *Zh. Prikl. Khim.*, 1996, vol. 69, no. 11, pp. 1917–1920.
5. Trifonov, S.A., Sosnov, E.A., and Malygin, A.A., *Zh. Prikl. Khim.*, 2004, vol. 77, no. 11, pp. 1872–1876.
6. Rychkov, A.A., Trifonov, S.A., Kuznetsov, A.E., et al., *Zh. Prikl. Khim.*, 2007, vol. 80, no. 3, pp. 463–467.
7. Trifonov, S.A., Sosnov, E.A., Belova, Yu.S., et al., Zh.

Prikl. Khim., 2007, vol. 80, no. 8, pp. 1374–1379.

8. Balandina, V.A., Gurevich, D.B., Kleshcheva, M.S., et al., *Analiz polimerizatsionnykh plastmass* (Analysis of Polymerization Plastics), Leningrad: Khimiya, 1967.
9. Muzgin, V.N., Khalezina, L.B., Zolotavin, V.A., et al., *Analiticheskaya khimiya vanadiya* (Analytical Chemistry of Vanadium), Moscow: Nauka, 1981.
10. Fowkes, F.M., *Ind. Eng. Chem*., 1964, vol. 56, no. 12, pp. 40–52.
11. Mel'nikova, N.B., Ignatov, V.I., Dolzhikova, V.D., and Summ, B.D., *Vestn. Mosk. Gos. Univ., Ser. 2: Khim*., 1998, vol. 39, no. 6, pp. 413–417.
12. Magonov, S.N., Elings, V., and Whangbo, M.-H., *Surf. Sci*., 1997, vol. 375, nos. 2–3, pp. 385–391.
13. Polyakov, A.V., Duntov, F.I., Sofiev, A.E., et al., *Polietilen vysokogo davleniya: Nauchno-tekhnicheskie osnovy promyshlennogo sinteza* (Low-Density Polyethylene: Scientific and Technical Principles of Industrial Synthesis), Leningrad: Khimiya, 1988.
14. Minsker, K.S. and Fedoseeva, G.T., *Destruktsiya i stabilizatsiya polivinilkhlorida* (Degradation and Stabilization of Polyvinyl Chloride), Moscow: Khimiya, 1979.
15. Van Oss, C.J., Chaudhury, M.K., and Good, R.J., *Chem. Rev.*, 1988, vol. 88, pp. 927–941.
16. Van Oss, C.J., Good, R.J., and Chaudhury, M.K., *Langmuir*, 1988, vol. 4, pp. 884–891.
17. Van Wazer, I.R., *Phosphorus and Its Compounds*, New York: Wiley–Interscience, 1958.