Soiling of Plasticized Poly(vinyl chloride)

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Received 20 November 2006; accepted 17 January 2007
DOI 10.1002/app.26283
Published online 17 May 2007 in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: The effects of three plasticizers and two plasticizer concentrations on the topography and soiling of poly (vinyl chloride) (PVC) were studied. Palmitic acid and triolein were chosen to represent solid and liquid soils. The feasibility of using infrared spectroscopy to quantify the amount of soil on PVC was examined. The structure of the solid model soil on plasticized PVC was studied with optical microscopy and atomic force microscopy. Palmitic acid formed two different structures on the PVC surface. Both the type and concentration of the plasticizer influenced the structure of the oily soil on plasticized PVC. The wetting of plasticized PVC with the liquid oily soil was compared to wetting with water through the measurement of the contact angles. Plasticized PVC was hydrophobic and oleophilic. © 2007 Wiley Periodicals, Inc. J Appl Polym Sci 105: 3047–3053, 2007

Key words: injection molding; poly(vinyl chloride) (PVC); surfaces

INTRODUCTION

Poly(vinyl chloride) (PVC) is a widely used, low-cost thermoplastic that is easily modified. PVC is also a hard polymer and difficult to mold, and it begins to degrade at processing temperatures. Various additives are employed to facilitate the processing and prevent degradation. Moreover, plasticizers, stabilizers, fillers, extenders, lubricants, antioxidants, and dyes are added to modify the properties of PVC products.[1,2] The multicomponent formulations of commercial PVC products make it difficult to single out the effect of a single component.

The soiling of PVC is greatly affected by plasticizers. Plasticizers tend to solubilize soils and ease their migration into the wear layer,[3] so the removal of the soil afterwards is difficult. Soil-resistant coatings are applied as a means of overcoming this problem. Less plasticized PVC,[4] urethanes, acrylics, acrylic blends, acrylic–vinyl blends, and polyesters may be applied.[5] The soil resistance of PVC floor coatings has also been improved by UV-curing trifunctional urethane acrylate and acrylate monomers containing carboxylic acid groups.[6] In addition to soil resistance, UV-curing coatings have good scratch and abrasion resistance.[7] The soil resistance of PVC can also be enhanced through compounding with a soil-resistant plasticizer. Benzoate plasticizers have been suggested for use in resilient flooring to improve soil resistance and UV stability.[8,9]

Both the multicomponent formulations of PVC and the soiling process itself are complex. Soil can be solid, liquid, or a combination of these. Model soil compounds that simulate real dirt but whose chemistry is simple are used to investigate the soiling phenomenon. Fatty acids and triglycerides are the main components in human-based sebum and natural oils and make suitable model compounds for the study of soiling with oily substances. Both have been widely used in detergency and soiling studies of solid surfaces.[10–16] An examination of the wetting properties of liquid triglycerides can help us in understanding the interactions between oily soil and solid surfaces.[17–19]

Given the widespread use of PVC, its soiling has economic and aesthetic importance as well. To understand the soiling of PVC and the relationship between PVC and its additives and soiling, the formulation of PVC needs to be kept as simple as possible. The first step in soiling studies is to examine the soiling of pure PVC.[20] The additives can then be added one by one, and the differences in the soiling of pure and doped PVCs can be examined. In this study, the effects of a plasticizer and its concentration on the structure of a solid oily soil on PVC surfaces were studied with the use of palmitic acid as a model soil. The wetting and soiling properties of plasticized PVC were examined through the measurements of the contact angles of deionized water and a liquid triglyceride, triolein. Because the addition of a stabilizer is essential to prevent the degradation of PVC during processing,[21] the PVC samples contained a stabilizer as well as a plasticizer.

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Contract grant sponsor: Finnish Funding Agency for Technology and Innovation.

TABLE I
Compositions and Codes of PVC (S 98) Samples

Sample	Plasticizer	Plasticizer concentration (wt %)
Benzo20	Benzoflex 2088	20
Benzo30	Benzoflex 2088	30
DOP20	DOP	20
DOP30	DOP	30
Hexa20	Hexamoll DINCH	20
Hexa30	Hexamoll DINCH	30

The amount of the stabilizer (Therm-Chek 7500L) was constant (3 wt %) in every sample.

EXPERIMENTAL

Preparation of the PVC samples

PVC (S 98, Dynea, Porvoo, Finland) powder was dry-blended with 3 wt % liquid stabilizer (7500L, Therm-Chek, Ferro, Louvain-la-Neuve, Belgium) in a Henschel mixer (FM 10 L, 800726). When the temperature reached 60°C, the plasticizer (20 or 30 wt %) was added gradually. Three different plasticizers were tested: Benzoflex 2088, diisononyl cyclohexane 1,2-dicarboxylate (Hexamoll DINCH), and dioctyl phthalate (DOP). The codes and compositions of the PVC samples are presented in Table I. The amount of the stabilizer was the same in all samples, whereas the amount of the plasticizer varied. The chemical compositions and manufacturers of the stabilizer and plasticizers are presented in Table II. Mixing was continued until the temperature reached 80–90°C, after which the blend was allowed to cool.

PVC–stabilizer–plasticizer blends were granulated with a DSM Midi 2000 extruder and a grainer (Geleen, The Netherlands). Granulated blends were injection-molded by an Arburg Allrounder 270S 350-150 injection molding system (Lossburg, Germany). The injection-molded samples were disks with a diameter of 2.5 cm and a thickness of 2 mm.

Soiling and characterization of the PVC samples

PVC samples were soiled by a spin-coating technique. The palmitic acid (99%; Aldrich, Steinheim, Germany), used as a solid model soil, was dissolved in 1-propanol before being applied to the sample. The sample was then rotated in a spinner at 2000 rpm for 3 min. The concentrations of the soil solutions were 20 and 50 mg/mL.

Infrared (IR) spectroscopy measurements were carried out with a Nicolet Avatar 320 Fourier transform infrared spectrometer (Madison, IL) to determine the quantity of palmitic acid on the PVC surfaces. Optical microscopy (BX-51, Olympus, Nagano, Japan) and atomic force microscopy (AFM; Explorer 4400-11, Thermo Microscopes, Sunnyvale, CA) examinations were made before and after soiling. The samples were photographed with the optical microscope in normal light. AFM images were measured in a noncontact mode.

Contact angles of water and triolein on PVC surfaces were determined with a KSV Cam200 (Helsinki, Finland) to reveal the wetting properties of the surfaces. A deionized water drop (5 μL) or a triolein drop (>97%; Fluka, Buchs, Switzerland; 2 μL) was placed on the surface and imaged for 30 s. Images were taken at 1-s intervals. The water contact angles were obtained as averages of values recorded between 15 and 29 s, and the triolein contact angles were recorded as averages of values recorded between 20 and 29 s. Sixteen replicate measurements were made for water, and 16 were made for triolein.

RESULTS AND DISCUSSION

The model soil compound was deposited onto PVC samples by a spin-coating technique. The dissolved model soil was spread over the surface, and the solvent evaporated. The thickness of the soil layer that formed on the sample surface depended solely on the concentration of the solution and rotation speed. It was independent of the amount of the soil solution applied to the sample surface because the excess solution flew off during sample rotation. The amount of the soil solution needed to be sufficient, however, as otherwise the soil layer would not cover the entire surface.

Quantification of soil on plasticized PVC

Quantifying the exact amount of soil on the PVC surface would be beneficial in studying the soiling of surfaces. A radiochemical method[12,22] and colorime-

TABLE II
Chemical Compositions and Manufacturers of PVC Additives

Additive	Composition	Manufacturer
Therm-Chek 7500L	Calcium/zinc complex mixture	Ferro (Louvain-la-Neuve, Belgium)
Benzoflex 2088	61–69% diethylene glycol dibenzoate, 16–24% dipropylene glycol dibenzoate, and 11–19% triethylene glycol dibenzoate	Velsicol (Rosemont, IL)
DOP	Dioctyl phthalate	Borealis (Porvoo, Finland)
Hexamoll DINCH	Diisononyl cyclohexane 1,2-dicarboxylate	BASF (Ludwigshafen, Deutschland)

try[23,24] have been applied, but both have the disadvantage of requiring a tracer: in the radiochemical method, a radioactive compound such as a ^{51}Cr- or ^{14}C-labeled compound, and in colorimetry, a dye such as carbon black. Ellipsometry has been proven to be a good method for determining the amount of soil released from PVC in a detergency process,[11–14] but the exact amount of soil on the original surface is difficult to determine because of the low refractivity of PVC and the similarity of the refractive indices of PVC and triglycerides.[12]

IR spectroscopy measurements allow the amount of soil on unplasticized PVC to be determined without a tracer.[20] IR measurements have also been used in detergency studies of nonionic surfactants and tristearin.[10] The IR vibration due to the C=O stretching of palmitic acid was 1699 cm^{-1}. The C=O stretching of the plasticizer caused the vibration around 1720 cm^{-1}. Because the soil layer on PVC was thin and the amount of palmitic acid was small compared with the amount of the plasticizer, the C=O stretching of the plasticizer hid the vibration of palmitic acid. The vibration of palmitic acid was not brought out on plasticized PVC, not even by additional treatments of the spectra.

Structure of soil on plasticized PVC

Optical microscopy and AFM allow nonconducting samples to be examined without a pretreatment and are suitable for analyzing polymer surfaces with and without model soil coatings. Optical microscopy has been used to study the polymorphism and crystallization kinetics of tripalmitin.[25] AFM has been used to study PVC surfaces, such as the surface topography of solvent-cast PVC films,[26] the topography of unplasticized PVC before and after soiling of the surface,[20] and the topography of commercial PVC tiles.[27]

In this study, optical microscopy and AFM measurements were used as supportive methods to study the effects of the type and concentration of the plasticizer on the topography of the PVC surface. In addition, a study was made of the spreading and structures of palmitic acid coatings on PVC surfaces. AFM measurements were performed in a noncontact mode in which the cantilever vibrated near the surface without physical contact between the tip and the sample. The noncontact mode is suitable for deposited samples because it does not damage soft surfaces.

Optical microscopy did not reveal any differences on plasticized PVC surfaces due to the type or concentration of the plasticizer. According to AFM, the surfaces were smooth. The height differences in an area of 0.01 mm^2 were between 60 and 90 nm on Benzo, DOP20, and Hexa20 surfaces, whereas DOP30 and Hexa30 surfaces were slightly rougher. The topographies of PVC surfaces plasticized with Benzoflex 2088 or DOP were similar and unaffected by the plasticizer concentration. The topography of the Hexa surfaces differed, as can be seen in Figure 1.

Optical micrographs of soiled PVC surfaces are shown in Figure 2. Palmitic acid formed mainly two kinds of structures on the surfaces. One structure appeared as smooth and roundish areas. Between these smooth areas, crystals of palmitic acid were formed, which can be seen as dark spots in Figure 2. Both the type and concentration of the plasticizer influenced the ratio of smooth areas to crystalline areas. The crystals were largest and most dispersed on the Benzo20 surface. The crystals on the DOP20 surface were similar to those on the Benzo20 surface but less dispersed, whereas on Hexa20, the crystals were much smaller and organized as lines. The crystals were more powdery on surfaces containing 30% plasticizer than on surfaces containing 20% plasticizer, but the same trend for their size was observed.

On surfaces containing 30% plasticizer, thin cracks could be seen on smooth palmitic acid areas. The cracks were observed also on Hexa20 surfaces but not on Benzo20 or DOP20 surfaces. AFM measurements showed the cracks to consist of small, ordered palmitic acid crystals, such as those shown in Figure 3(c). Figure 3(a) shows the platelike structures of palmitic acid on the Benzo20 surface. A similar structure was observed on unplasticized PVC.[20] As the concentration of the deposition solution increased, the thickness of the plates grew as well, and the number of palmitic acid crystals increased, as seen on the DOP20 surface coated with a 50 mg/mL palmitic acid solution [Fig. 3(b)].

Wetting of plasticized PVC surfaces

The contact angles of water and triolein on plasticized PVC are presented in Table III. The water contact angles varied between 66 and 83°, indicating that plasticized PVC is slightly hydrophobic. The water contact angles on DOP and Hexa surfaces were very similar and independent of the plasticizer concentration. In the case of Benzoflex 2088, the water contact angle decreased with an increase in the plasticizer concentration. The behavior of water on plasticized PVC surfaces can be explained by the chemical structures of the plasticizers. DOP and Hexamoll DINCH contain long hydrocarbon chains making the plasticized PVC surface hydrophobic. Because unplasticized PVC is a hydrophobic material as well, the concentration of the plasticizer has no effect on the wetting properties of PVC in that case. Different glycol dibenzoates (Benzoflex 2088) contain a lot of oxygen in their structure, and when the plasticizer concentration increases, the amount of oxygen on the plasticized PVC surface increases as well and makes the wetting of the surface easier.

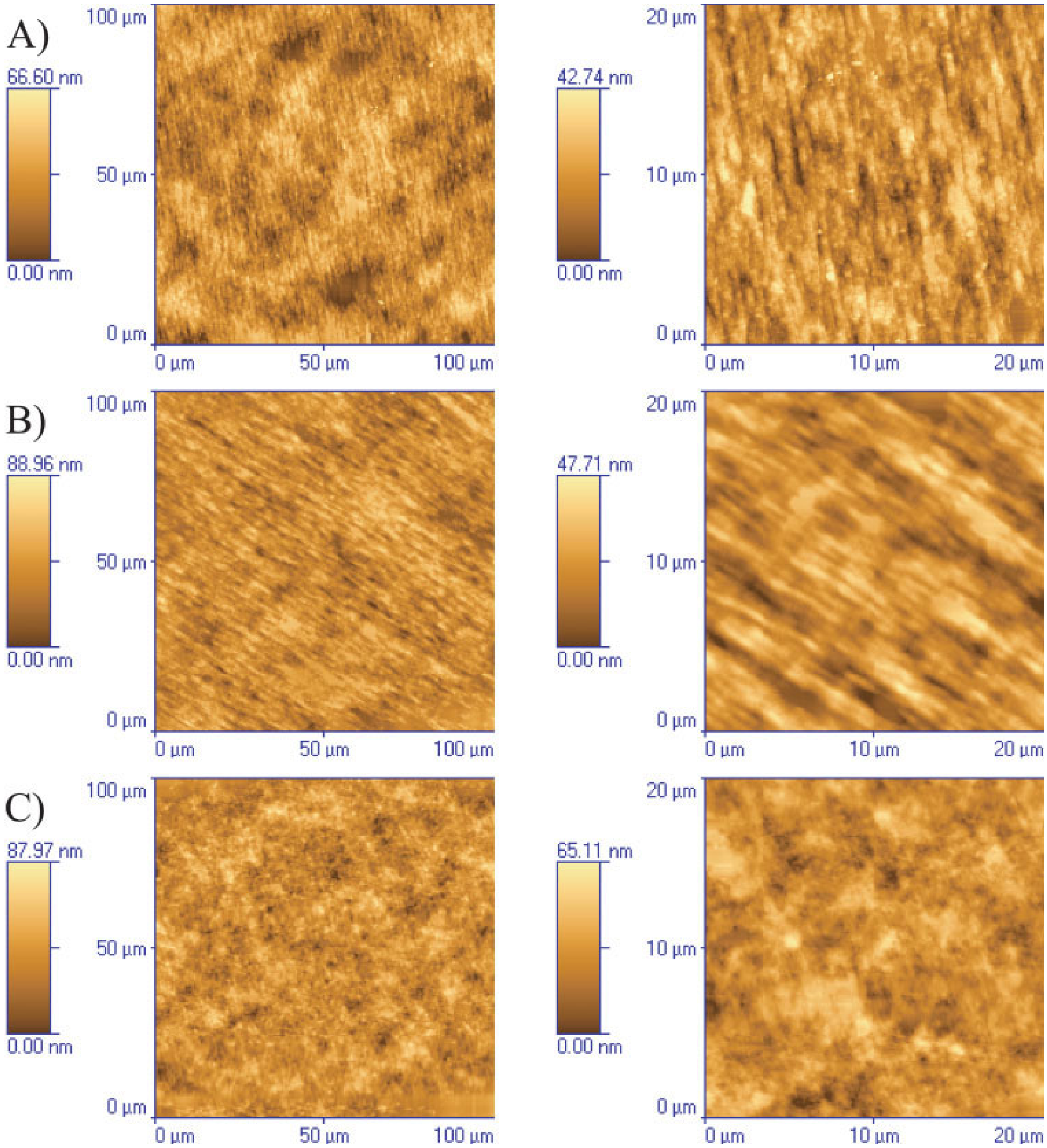

Figure 1 Topography of smooth PVC surfaces containing 20% plasticizer (studied by noncontact AFM): (A) Benzo20, (B) DOP20, and (C) Hexa20. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

All plasticized PVC surfaces were oleophilic and significantly wetted by triolein. The plasticizer concentration influenced the contact angle of triolein; PVC containing more plasticizer became more wetted by the liquid oily soil. There was also a difference between the plasticizers: Benzo surfaces were less wetted and Hexa surfaces were more wetted by triolein. The differences between the plasticizers were more significant on surfaces containing 20% plasticizer than on surfaces containing 30% plasticizer.

Our earlier cleanability studies[28] made on plasticized PVC surfaces showed the difficulty of removing triolein from surfaces. The removal of triolein was sensitive to both the type and concentration of the plasticizer. Oily soil was most easily cleaned from PVC containing the benzoate plasticizer, although we note that the benzoate composition used in the cleanability studies was different from that of this study. Because the highest contact angle for triolein in this study was that for the Benzo surface, however, the same trend appears to hold in this study as in the earlier study.

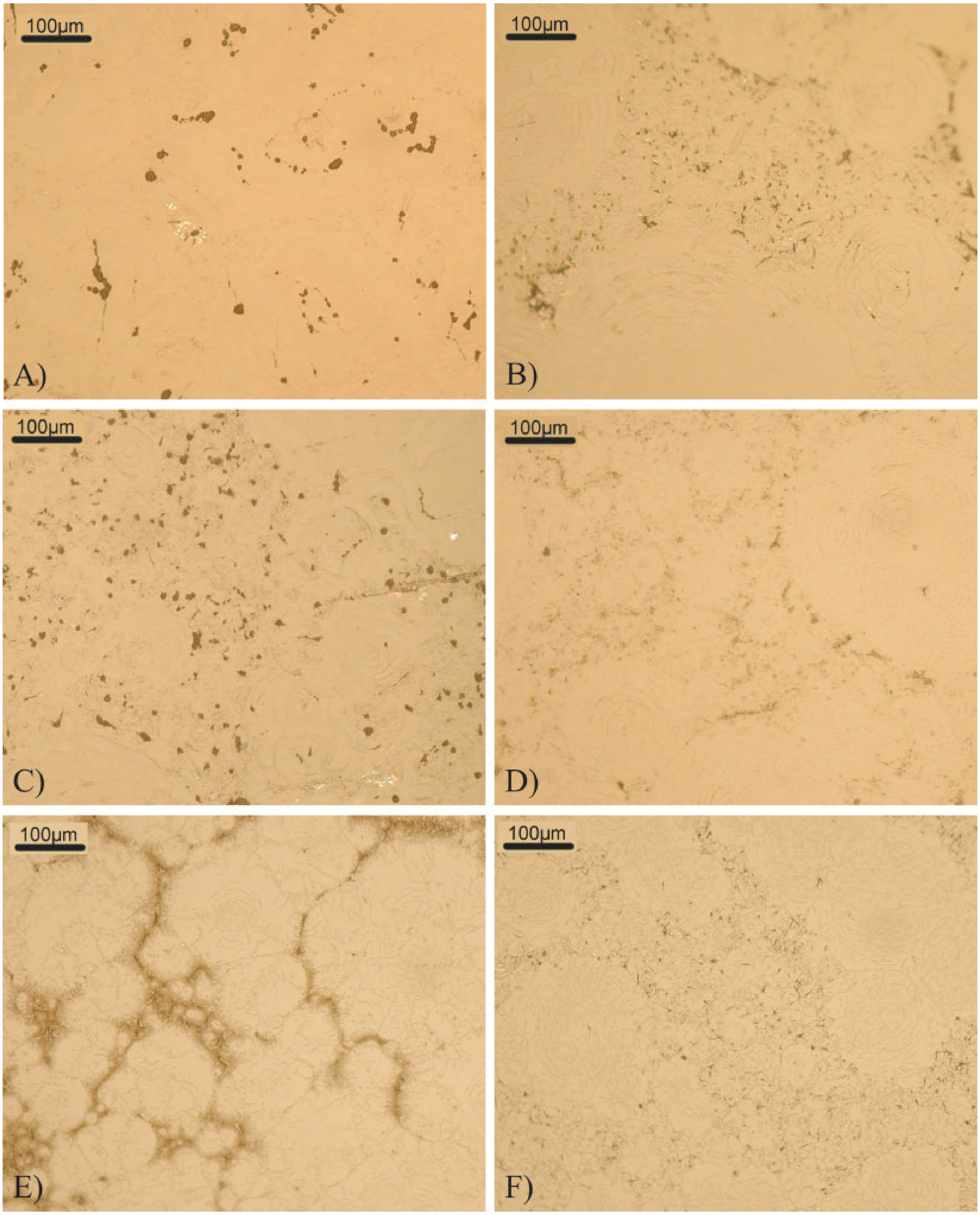

Figure 2 Structure of palmitic acid coatings on PVC surfaces containing different plasticizers and plasticizer concentrations (studied by optical microscopy): (A) Benzo20, (B) Benzo30, (C) DOP20, (D) DOP30, (E) Hexa20, and (F) Hexa30. The surfaces were coated with palmitic acid at a concentration in solution of 50 mg/mL. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

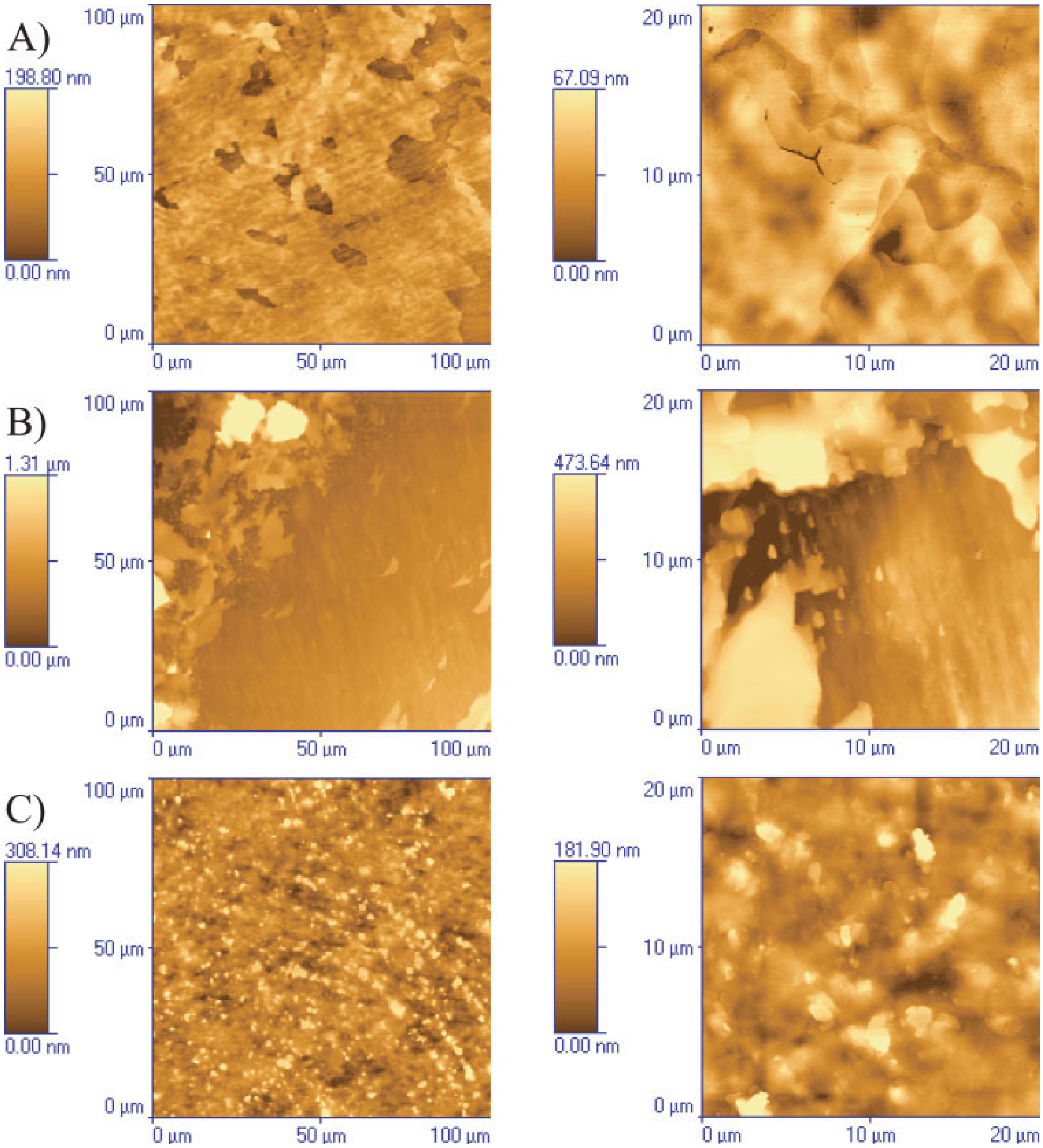

Figure 3 Structure of palmitic acid coatings on surfaces of PVC containing 20% plasticizer (the surfaces were studied by noncontact AFM, and two magnifications are presented): (A) Benzo20 surface soiled with a 20 mg/mL palmitic acid solution, (B) DOP20 surface, and (C) Hexa20 surface soiled with a 50 mg/mL palmitic acid solution. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

CONCLUSIONS

The plasticized PVC surfaces were smooth. According to AFM measurements, the topography was not greatly influenced by the type or concentration of the plasticizer. Plasticizers contain abundant C=O groups, which prevent the use of C=O stretching vibrations of palmitic acid to quantify the amount of palmitic acid on the plasticized surface.

Both the type and concentration of the plasticizer influenced the structure of oily soil on plasticized PVC. Optical microscopy and AFM measurements showed there to be two different areas on PVC soiled with palmitic acid. One area consisted of a relatively smooth, platelike palmitic acid layer, and the other consisted of crystalline palmitic acid. The ratio of the relatively smooth area to the crystalline area mostly depended on the plasticizer concentration. According

TABLE III
Contact Angles and Their Standard Deviations on Plasticized PVC Surfaces

Sample	Water contact angle (°)	Triolein contact angle (°)
Benzo20	79.0 ± 1.9	19.3 ± 3.7
Benzo30	66.4 ± 1.9	13.9 ± 1.5
DOP20	81.2 ± 1.6	16.4 ± 1.7
DOP30	81.8 ± 1.1	13.7 ± 0.7
Hexa20	81.3 ± 0.9	15.8 ± 1.3
Hexa30	82.8 ± 1.0	12.6 ± 0.8

to wetting studies, the plasticized PVC surfaces were hydrophobic and oleophilic. The plasticizer type or concentration did not influence the hydrophobicity of PVC, except in the case of Benzoflex 2088. When the Benzoflex 2088 concentration increased, the water contact angle decreased. The increase in the plasticizer concentration increased the oleophilicity of plasticized PVC.

This study was part of the Clean Surfaces 2002–2006 Technology Program.

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