



Surface characterization of industrial flexible polyvinyl(chloride) films



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ABSTRACT

Surface properties of industrial coated plasticized PVC flooring films have been investigated, with the aim of establishing possible additives migration, which causes chemical surface modification of the film and consequently its adhesion behavior. The storage period, from the production time to the converting operations (printing, laminating...) can also promote the additives migration. The surface of these films was extracted with acetone and water and the organic fraction was identified by surface tension, FTIR and GC/MS. These techniques established clearly that the extracted molecules are issuing from the plasticizers. Virgin and aged films were characterized by contact angle measurement and the surface chemistry was directly studied by XPS analyses. The first technique showed stable wettability properties of the films during storage. The contact angle of water droplet was found to decrease step wisely indicating that some surfactant-type molecules were extracted during the measurements, as confirmed by surface tension measurements. XPS established that a higher concentration of the chlorine-free additives was localized on the surface, which points out a probable enrichment of the surface by the plasticizers and the other additives. This suggests that migration kinetic of plasticizers is very high during the production, because of the high processing temperature.

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1. Introduction

Flexible polyvinyl(chloride) (PVC) films are used in a multi-plex of commodity products, which cover a variety of applications. In each case, specific films properties are needed to fulfill the expected requirements, thus implying the use of many chemical additives and aids. The most commonly used families are plasticizers, heat stabilizers and process aids additives (lubricant, rheology modifiers...). The amount of these additives can reach to 50% weight by weight of the film composition. As in any multi-component formulation, the introduced additives are small size (to compare with the matrix) and possessing high mobility. As a consequence, diffusion mechanisms can cause their migration toward the film surface. These mechanisms result in random movements of the molecules and are driven by thermal agitation i.e. Brownian motion. This migration phenomenon is well known for polymer and has been described by many authors for PVC, in particular, [1–3]. It depends mainly on additive molecule structure (size, flexibility, architecture) [4], its affinity with the matrix and the rest of formulation ingredients, but also on the environment parameters as temperature and relative humidity [5].

Most of the studies were focused on sanitary issue particularly food-contact films [6,7], and medical products [8,9], in order to assess their interaction with bodies in which they are in contact, e.g. additives migration into food, water, blood, ... Other authors showed the influence of the formulation composition on the films surface properties [10] and its printability [11–13]. We have focused on papers dealing with the surface properties of PVC and its printability behavior. In this context and to the best of our knowledge, only two papers have been dealing with commercial products [11,12]; whereas two other ones dealt with academic research aiming at optimizing PVC formulations [10], [13]. Moreover, several authors have used simplified (or even model) formulations. Therefore, if one takes into account the wide range of commercial films (mostly based on empirical optimization of the formulation composition), then it is very hard to find papers in which industrial PVCs were systematically studied in terms of surface properties and their incidence on their printability features. Moreover, the surface of these films is subjected to a rapid evolution (as mentioned above, the migration of small molecules), which could play a relevant role concerning the adhesion properties of the ensuing aged PVC surface. These statements motivated us to undertake a systematic characterization of an industrial PVC film, as well as the main components constituting it.

Thus, in this paper, surface properties of industrially made flexible PVC films have been investigated. To manufacture PVC

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Table 1
The plastisol formulation tested here.

Component	Quantities (phr)
PVC Resin	100
Plasticizer A	39
Plasticizer B	17
Lubricant	2
Heat stabilizer	3
Co-stabilizer	4
Mineral fillers	91

films, a nonwoven glass fibers mat is impregnated-coated by liquid plastisol and the resulting film is thermally treated to form the matrix network. Then, the film web is wound and the rolls are stored before being printed or laminated. Depending on the production flow, the storage time may vary from few hours to one month. The aim of this paper is to investigate the physico-chemical characteristics of the films within the aging time, in order to ascertain their possible modification during storage. For this purpose, the surface free energy evolution of the films has been examined during aging, and analyses have been carried out to establish the chemical composition of the surface of the films.

2. Materials and methods

2.1. Sample media manufacturing

Sample media are composite films made of nonwoven glass-fiber embedded in a plastisol matrix. The plastisol is a dispersion of polyvinylchloride (PVC) powder in plasticizers and additives. The plastisol was prepared in an industrial mill and its formulation is described in Table 1. Quantities are classically expressed in weight per weight on the basis of hundred parts of resin (phr).

Samples were industrially prepared by impregnating the nonwoven glass-fiber with the plastisol slurry using a blade coater and by consolidating the subsequent composite by heating at 180–200 °C, during around 1 min [14]. The tested samples were withdrawn at very short time after the production and left to be aged for 42 days, under controlled conditions (i.e., at 23 °C and 50% HR). In fact, they were left to reach a total stabilisation.

2.2. Contact angle

Contact angles have been measured using a Dataphysics SCA 20 goniometer. The used liquids and their relevant properties are reported in Table 2.

The considered values are the average of five measurements on each sample and for each liquid. These values were processed according to Owens–Wendt method [15], in order to deduce the surface energy parameters.

2.3. Extraction procedure

Film surfaces were washed with solvent (acetone and water) in order to extract the chemical components present at the surface as physically adsorbed molecules. Acetone was pulverized at the

Table 2
Surface tension of the liquids (mJ/m², at 25 °C).

Solvents	γ^{tot}	γ^{d}	γ^{p}
Water	72.1	19.9	52.2
Formamide	56.9	23.5	33.4
Glycerol	64.0	34.0	30.0
2-Ethanol amine	48.9	31.5	17.4
Hexadecane	27.5	27.5	0.0

film surface at room temperature and then collected immediately (probably after few seconds of contact with the surface) and analyzed, in order to identify the acetone-extracted molecules. Water extraction was achieved by adding around 100 mL at the surface of PVC films and left 48 h in contact with the surface of the film. The recovered water-extracted molecules liquid was then analyzed.

2.4. Fourier Transform Infrared Spectroscopy (FTIR)

FTIR spectra of samples were collected using a PerkinElmer Spectrometer Paragon 1000 in transmission mode. Liquid samples were assessed using NaCl pellets (CaF₂ pellets for water containing products), from 4000 to 500 cm⁻¹ and with a resolution of 4 cm⁻¹. Each spectrum represents an average of 20 consecutive scans.

2.5. Gas chromatography coupled mass spectrometry (GC/MS)

GC–MS analysis was carried out with an Agilent Technologies (Waldbronn, Germany) 6850N GC coupled to an Agilent Technologies 5975 inert XL Mass Selective Detector (MSD). The GC housed a fused silica capillary column (Agilent 19091S-433E, 30 m × 0.25 mm i.d., 0.25 μm film thickness) interfaced directly to the ions source of the MSD. The carrier gas was helium at a flow rate of 20 mL min⁻¹. The injector temperature was 300 °C. The initial column temperature was set at 50 °C and, after 2 min the temperature was increased at a rate of 25 °C min⁻¹ to 300 °C, which was held for 3 min (post-run). For the additives determination, the MSD was operated in the selected ion monitoring (SIM) mode. The energy of the electron beam was 70 eV.

2.6. X-ray photoelectron spectroscopy (XPS)

The X-ray photoelectron spectroscopy (XPS) analyses were carried out in a Vacuum Generator XR3E2 apparatus with Mg K α X-ray source at 15 kV and 20 mA operating conditions. Analyses were carried out at an angle of 90° between the sample surface and the hemispherical analyzer. Pressure in the sample chamber was less than 10⁻⁸ Pa. Sample dimensions were 1 cm × 1 cm and the analyzed average area was about 40 mm².

Low resolution spectra, from 0 to 1100 eV binding energy, were collected with a data rate of 2 points per eV, and signal-averaged over three scans. The high-resolution spectra were collected with a data rate of 10 points per eV and signal-averaged over 20 scans. The pass energy was set at 30 eV for both low and high-resolution spectra resulting in an energy resolution of approximately 0.1 eV. The electron binding energy scale was calibrated by setting the C1s peak of graphitized carbon at 284.6 eV. Spectra were analyzed using a freeware software package, Fitt1.2 (GTK) (Photoelectron Spectroscopy Lab, Seoul National University) with Shirley background corrections.

An estimation of the elemental composition (atomic ratios) of the samples was obtained from the areas of the characteristic photoelectron lines after subtraction of a Shirley background, divided by the sensitivity factor.

Binding energy values were chosen from data available in the literature [16,17]. The Gaussian–Lorentzian peak shape mixing ratio was determined by the fit of the Au4f peak from a clean gold sample. Hence one can expect, for the major photoelectron lines, a relative accuracy of 1% on the calculated ratios.

3. Results and discussion

Industrial PVC films were sampled at the output of the coating process and the sampled films were then conditioned at 23 °C and 50% relative humidity (RH). These conditions were selected

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