

# An XPS Study of Different Polyvinylalcohol Films' Surface Composition

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## SYNOPSIS

Differences in surface chemical composition were found when examining poly(vinylacetate-co-vinylalcohol) (PVOH) film surfaces. The content of the acetate groups increased at the outermost surface when dried in air and similar content, when dried against a glass surface, compared to the bulk content. The enrichment varied from 200–1300%, as compared to the bulk content. The enrichment of the acetate groups was studied with X-ray photo electron spectroscopy (XPS or ESCA) at different analyzing angles. The bulk content was measured with Nuclear Magnetic Resonance spectrometry (NMR). © 1993 John Wiley & Sons, Inc.

## INTRODUCTION

Surface properties, such as adhesion and wettability, depend on the outermost surface chemical composition. Most often, the surface composition is different from the bulk, due to interactions with the surrounding environment, such as air or mold surfaces. The effect of the environment on polymer surfaces has been studied by several authors for both thermosets<sup>1-3</sup> and thermoplastics.<sup>4-9</sup>

The enrichment of components does not only involve mobile species, such as different additives and low molecular weight parts in the polymer, but it can also involve the polymer itself, which can contain both nonpolar and polar segments. Copolymers and polymer blends are materials with such properties. The main driving force for surface rearrangement is a difference in surface energy between the surface of the mold and the polymer.

In compression molding of thermosets and thermoplastics, for example, a release agent, a release film, or a peel-ply is often used for easy removal and protection of the plastic parts. The outermost mold surface (i.e., a release surface) interacts with the polymer surface, influencing the chemical composition. The change in composition can be a result of

the polymer itself, by enrichment of different components, and of contamination from the mold. The polymer surface is often contaminated, which changes the surface properties, such as adhesion and wettability, as compared to the bulk properties of the polymer. To improve the adhesion strength, it is often essential that the weak boundary layer, if present, is removed.

One example, in which the removal of contaminants is extremely important, is adhesive bonding of composites. If a release agent, that is, a silicone oil, is present, the joint strength will be low and mechanical or chemical pretreatments are used extensively to obtain composite surfaces suitable for bonding.<sup>10</sup> We have studied the possibilities of enriching functional groups at the surface using different release films, such as poly(ethylene terephthalate) (PET) and perfluorinated ethylene-propylene copolymer (FEP). Expecting an increase in the content of functional groups, which later can react with an adhesive, we also observed that the release films could cause contamination, which was considered to be an unwanted effect.

It should, however, be possible to use the contamination to improve the adhesive properties of the surface. Such contamination should be anchored at the surface by a reaction with the composite and should also contain groups that are capable of reacting with the adhesive. To avoid the formation of a weak boundary layer, it should also be possible to

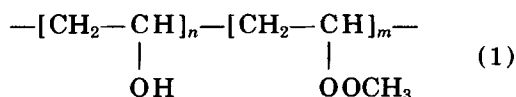
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remove the excess or nonbonded parts of the adhesive promoter. With respect to environmental issues, it is also an advantage if water can be used for washing. Water-soluble polymers, with reactive groups in the repeating unit, might fulfill these demands.

Polyvinyl alcohol (PVOH) is an interesting water soluble polymer for use as an adhesion promoter. This polymer is used in a number of applications, such as fibers, films, coatings, textile sizing, and as adhesives.<sup>11-12</sup> It is produced by hydrolysis of the polyvinyl acetate and commercial materials are, in most cases, copolymers of vinylalcohol and vinylacetate. The degree of hydrolysis controls many of its properties, among them the solubility. Being a copolymer, the surface composition of the PVOH might depend on the environment. In this article, we present the results of XPS measurements of PVOH surfaces obtained by casting in air. These surfaces will later be used as mold surfaces for an epoxy composite to introduce reactive groups at the surface.

## EXPERIMENTAL

Polyvinyl alcohols with different molecular weights, ranging from  $M_w = 15,000$  to  $224,000$ , and with different contents of hydroxyl groups, were used (see Table I). The polymers were dissolved in water with a content of 5% by weight. Films were cast on a clean glass surface and were dried for 12 h at  $50^\circ\text{C}$ . The films were then removed from the glass surface for different analyses.



The polymer surfaces were analyzed with a Perkin-Elmer PHI 5500 ESCA system, with a monochromatic  $\text{Al}(\text{K}_\alpha)$  X-ray source, in an ultra-high vacuum (background pressure  $10^{-8}$ – $10^{-9}$  torr). The escaping electrons were counted as a function of the electrons'

kinetic energy. The sample was positioned at different angles with respect to the analyzer. The analyzed areas were  $1 \times 2$  mm, with an information depth of 1–10 nm. The build-up of positive charge 4–5 eV on the polymer surface was neutralized by electrons. PHI sensitivity factors, specific for this instrument, were used for calculations to determine the relative amount of the elements present ( $\text{C} = 1.00$ ,  $\text{O} = 2.40$ ). A graphics terminal was used for the curve fit, with Gaussian–Lorentzian peaks and intergrated background.

To determine the content of the acetate groups, the copolymers were analyzed with  $^1\text{H}$ —NMR at 300 MHz, using a Varian WXR 300 spectrometer. The spectra were obtained from solutions in dimethylsulfoxide- $d_6$  at  $40^\circ\text{C}$ .

## RESULTS AND DISCUSSION

The bulk composition of the copolymers was determined with  $^1\text{H}$ —NMR. A typical spectrum is shown in Figure 1. The composition was calculated by comparing the area of the methine protons of PVOH at 3.83 ppm and the area of the methyl group in the vinyl acetate residues at the 1.92 ppm. The results are presented in Table II and they agree well with the data provided by suppliers.

The dominating fraction is thus poly(vinylalcohol) and it could be expected that the hydroxyls are the most frequent functional groups at the surface. In our earlier work,<sup>1</sup> we studied the way in which polar components of ethylene copolymers may be enriched at the surface, depending on the mold surface. In this case, the most polar group, hydroxyl, is the most abundant, since the less frequent ( $\text{---COOCH}_3$ ) acetate group has lower polarity.

To obtain information about the surface composition, we have used XPS. A survey spectrum is shown in Figure 2. From this spectrum, it is possible to calculate the content of oxygen and carbon. Theoretically, the content of oxygen and carbon is 33%, independent of the degree of hydrolysis, which

**Table I** Properties of Used Water-Soluble PVOH Polymers

Polymer	Hydrolysis (%)	$M_w$ (g/mol)	Supplier
Polyvinylalcohol (PVOH-15)	86	15,000	Fluka
Polyvinylalcohol (PVOH-45)	86	45,000	Fluka
Polyvinylalcohol (PVOH-100)	86	100,000	Fluka
Polyvinylalcohol (PVOH-224)	99	224,000	Hoescht

**Table II Comparison of Bulk Content and Surface Content, Measured with NMR and XPS, when Analyzing PVOH Films Dried Against Air**

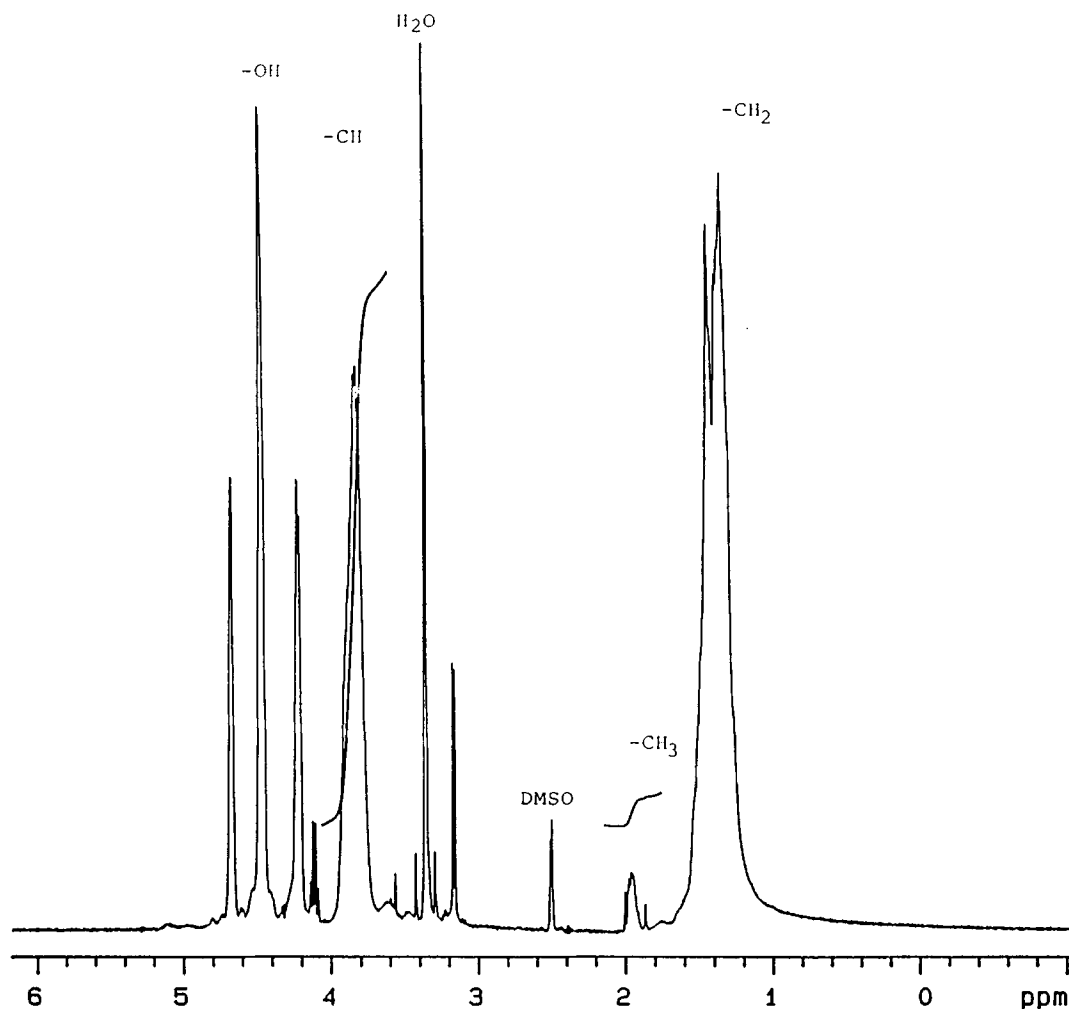
Polymer	Supplier	Acetate Content (mol %)	
		NMR	XPS ( $\theta = 45^\circ$ )
PVOH-15	14	14	43
PVOH-49	14	14	38
PVOH-100	14	14	31
PVOH-224	1	2	26

also was obtained for all samples within the experimental errors. The content of oxygen will thus not provide any information about possible enrichment.

More detailed information about the PVOH surface was instead obtained by curve fitting the C1s

XPS spectra to several carbon- and oxygen-containing structures. Figure 3 shows the C1s spectrum for a PVOH ( $M_w = 15,000$  g/mol) surface, obtained by drying against air. The broken line represents the results of the curve fitting, showing the position of the components. The binding energies for the components in the C1s spectrum were: 285 eV for  $\underline{C}-C$ ; 286.2 eV for  $\underline{C}-O$ ; 286.6 eV for  $\underline{C}-OH$ ; 289.2 eV for  $O-\underline{C}=O$ . Admittedly, the difference between  $C-OH$  and  $C-O$  is small, as compared to the resolution. However, the curve fitting is strengthened by the fact that the number of  $C-O$  structures, that is, methine carbons in the vinyl acetate residues, is the same as the amount of  $C=O$ . The composition of the different surfaces were evaluated from the curve fitted spectra.

In Table III are presented the results of the curve fitting procedure of the C1s spectra of the four



**Figure 1**  $^1\text{H}$ -NMR spectrum of PVOH 224,000 g/mol, solved in dimethylsulfoxide- $d_6$  (DMSO).

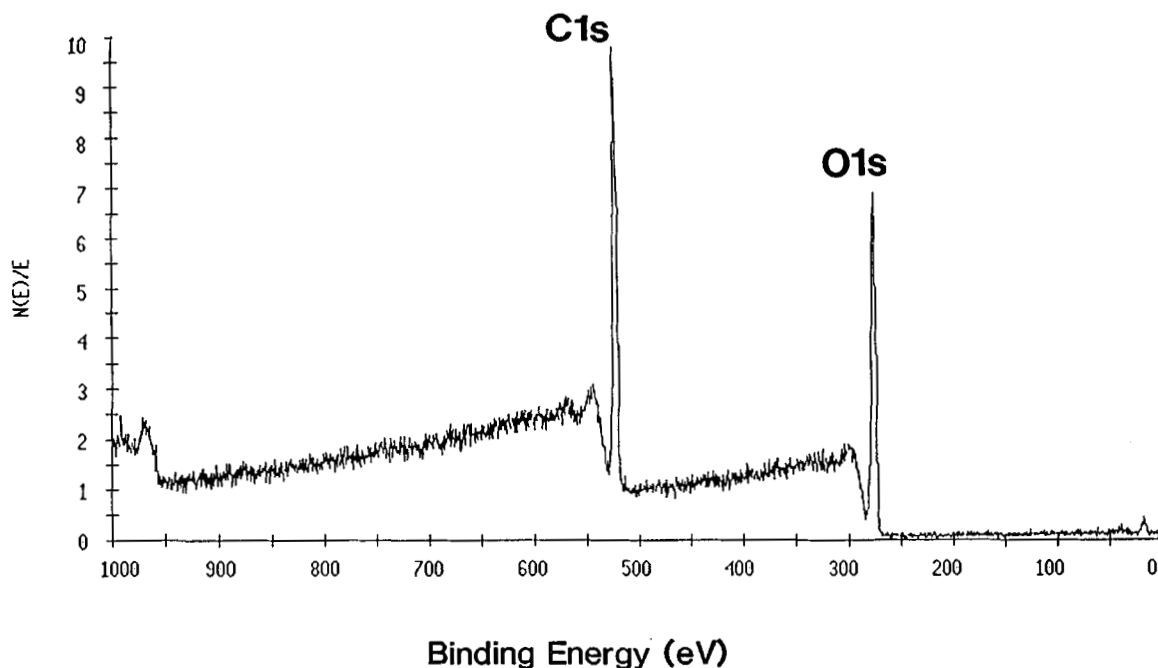


Figure 2 A XPS survey spectrum of PVOH 100,000 g/mol.

PVOH samples. A run, at an angle of  $80^\circ$ , was used, in addition to the normal angle of  $45^\circ$ . The former angle yields a lower surface sensitivity; the depth of information is *ca.* 90–100 Å for  $80^\circ$ , as compared to *ca.* 60–70 Å for  $45^\circ$ . The content of the acetate groups is much higher than the bulk composition for all samples. Considering the lower polarity of the acetate group, as compared to the hydroxyl group, an enrichment is expected when the surface

is formed in contact with a nonpolar medium, such as air. The enrichment of the acetate groups at the surface is due to the effort of the system to decrease the interfacial energy of the air-polymer interface.

The fraction of acetate groups, calculated from the XPS spectra obtained at  $45^\circ$ , is compared with the bulk concentrations in Table II. For the samples with a low degrees of hydrolysis (76%), the surface concentration of acetate is from 2–3 times higher

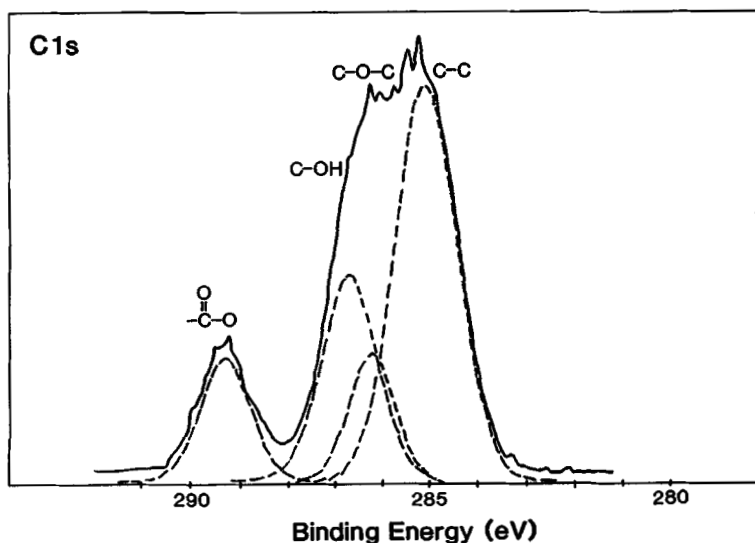


Figure 3 Curve-fitted C1s spectrum with different chemical components.

**Table III** Surface Composition of Different Polyvinylalcohol Films Molded Against Air

Take-off Angle/Surface	Total C1s Peak Area (%)			$\begin{array}{c} \text{O} \\ \diagup \\ \text{—C—} \\ \diagdown \\ \text{O—} \end{array}$
	—C—C—	—C—O—	—C—OH	
PVOH-15,000				
$\theta = 45^\circ$	47	16	22	14
$\theta = 80^\circ$	50	12	25	13
PVOH-49,000				
$\theta = 45^\circ$	48	15	23	14
$\theta = 80^\circ$	47	16	23	14
PVOH-100,000				
$\theta = 45^\circ$	47	11	29	13
$\theta = 80^\circ$	47	13	28	12
PVOH-224,000				
$\theta = 45^\circ$	56	10	25	9
$\theta = 80^\circ$	53	9	30	8

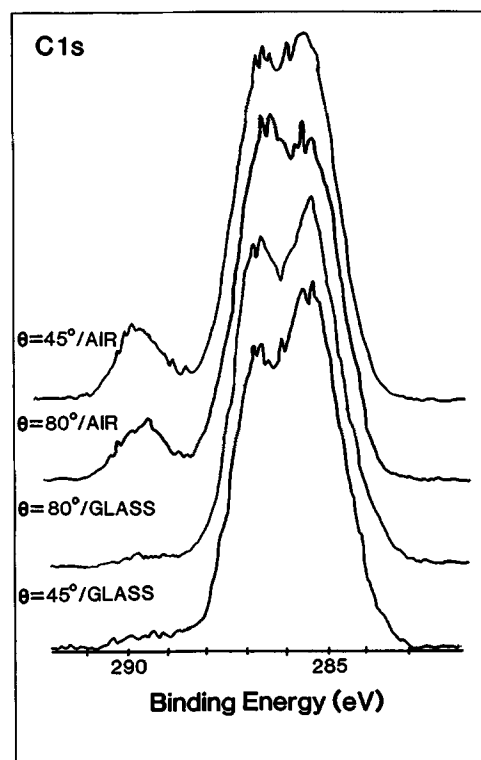
than the bulk content. The enrichment factor increases with decreasing molecular weight, which can be explained by the increased mobility. It should also be pointed out that all motion ceases when the water content decreases below that content having a glass transition at the drying temperature ( $50^\circ\text{C}$ ). With decreasing molecular weight, the critical water content decreases, which also should favor the enrichment of the nonpolar acetate groups.

The highest molecular weight sample ( $M_w = 224,000$ ) also has a much higher degree of hydrolysis (98%). Although the higher molecular weight should lead to lower mobility, the content of the acetate groups at the surfaces is as high as 26%, which is an enrichment factor of 13. The enrichment factors for the PVOH polymers are thus considerably higher than what was observed for the ethylene copolymers with vinylacetate or acrylic acid.<sup>1</sup> In the latter case, the polar groups could be enriched at the surface with a polar mold surface. The enrichment factor was only from 1.1–1.5, but these experiments were performed with melts, that is, the mobility was much lower than in the present experiments, in which films were made from solutions.

If data, obtained at the two take-off angles,  $45^\circ$  and  $80^\circ$ , are compared, a small decrease in the content of acetate groups can be seen for the higher angle (see Table III). This is reasonable when the high degree of enrichment is considered. The content of the acetate groups approaches the bulk content rapidly.

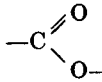
The surface of the PVOH-films, which had been in contact with the glass surface during casting, was

also analyzed in order to investigate the effect of a polar mold surface. In Figure 4, the C1s spectra ( $45^\circ$  and  $80^\circ$  take-off angle) of surfaces of PVOH-224,000, obtained against air and glass, are presented. The results of the curve-fitting procedure



**Figure 4** C1s spectra of PVOH-224,000, molded against glass and dried in air, analyzed at different take-off angles.

Table IV C1s Peak Compositions for Polyvinyl Alcohol PVOH-100,000 and PVOH-224,000

Take-off Angle/ Surface	Total C1s Peak Area (%)			
	-C-C-	-C-O-	-C-OH	
<b>PVOH-100,000</b>				
$\theta = 45^\circ/\text{Air}$	47	11	29	13
$\theta = 80^\circ/\text{Air}$	47	13	28	12
$\theta = 45^\circ/\text{Glass}$	47	5	42	6
$\theta = 80^\circ/\text{Glass}$	47	4	43	6
<b>PVOH-224,000</b>				
$\theta = 45^\circ/\text{Air}$	56	10	25	9
$\theta = 80^\circ/\text{Air}$	53	9	30	8
$\theta = 45^\circ/\text{Glass}$	57	2	40	1
$\theta = 80^\circ/\text{Glass}$	55	2	42	2

for this sample and for PVOH-100,000 are presented in Table IV.

The surface content of the acetate groups is much lower for surfaces obtained against glass. For PVOH-224,000, 3–4% was measured for the glass surface, as compared to 26% for the air surface. The composition is thus similar to the bulk, but there is still a certain degree of enrichment. The acetate groups have, however, a dual nature, in which the methyl group contributes to the nonpolar nature while the ester group is more polar and might interact with the silanol groups on the glass surface with hydrogen bonding. In the case of PVOH-100,000, the surface content of the acetate groups was similar to that of the bulk.

In conclusion, the surface content of acetate groups in films of PVOH is much higher than in the bulk when the films are cast from a water solution in air. With decreased molecular weight, the enrichment increases somewhat, while the degree of hydrolysis has a strong influence on the enrichment factor. In our continued work, we are using PVOH films, dried in air, as mold surfaces for epoxy composites. To anchor a layer of PVOH at the surface, the epoxy system should react with the hydroxyl groups of PVOH, and the enrichment of acetate groups may, therefore, be negative. The measurements of the PVOH surfaces obtained against glass showed, however, a much lower content of acetate groups. Considering the molding temperature ( $150^\circ$ ) and the softening effect of the epoxy resin, it is plausible that the PVOH surface can rearrange, leading to more surface hydroxyls and increased reactivity toward the epoxy system.

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