Permeation of Oxygen, Water Vapor, and Limonene through Printed and Unprinted Biaxially Oriented Polypropylene Films

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Oriented polypropylene (OPP) and coated OPP (acrylic/OPP/PVDC) films were printed with two commercially available inks to investigate the influence of inks on water vapor and oxygen transmission rates. The permeation of an aroma compound (*d*-limonene) through coated OPP film printed with these inks was also evaluated at 35 °C and 100% relative humidity. The water vapor transmission rate increased significantly through OPP film printed with nitrocellulose-based ink. The oxygen transmission rate was significantly lower through both OPP and coated OPP films printed with the nitrocellulose ink. The effect of inks on limonene permeation was minor compared to the marked increase in permeation measured when the PVDC side of the coated film was exposed to the aroma, compared to the acrylic side. Scanning electron micrographs of coated film cross sections revealed changes in film structure upon exposure to limonene vapors, which were most pronounced when the PVDC side was exposed to limonene.

Keywords: *Polypropylene; printing inks; oxygen transmission rate; water vapor transmission rate; limonene; film microstructure*

INTRODUCTION

Plastic films are used extensively in food packaging due to economic considerations and advantages in physical, mechanical, and chemical properties over other packaging materials. However, oxygen, moisture, and aroma compounds may permeate plastic packaging materials during storage, resulting in a loss of food quality. For example, oxygen ingress may cause rancidity in lipid-containing foods or oxidative degradation, which may cause other quality defects, particularly in flavor or color. Undesirable aroma compounds may diffuse into a package, or desired aromas may diffuse out of a package, thereby affecting the sensory quality of food (*1*, *2*).

The nature of interactions between penetrants and the polymer matrix dictate how penetrants are sorbed and dispersed throughout the polymer matrix (*3*, *4*). Sorption and diffusion of different permeant molecules, such as water or organic vapor, through polymeric films may affect the barrier and mechanical properties of the polymer.

Oriented polypropylene (OPP) is used in many food packaging applications because it provides an effective moisture barrier, high clarity, and gloss, as well as favorable mechanical properties, such as resistance to stretching, which contribute to stable converting qualities. Extensive research has been undertaken on the sorption and diffusion of penetrants through OPP. Taraiya et al. (*5*) showed that uniaxial and biaxial orientation of polypropylene reduced oxygen permeability of the film and that the drawing process (uniaxial and biaxial) reduced the amorphous nature of the film. They concluded that because diffusion has been shown to take place mainly through amorphous regions, a decrease in amorphous regions could be correlated to decreased oxygen permeability. In contrast, Moaddeb and Koros (*6*) reported that unoriented polypropylene had a lower equilibrium uptake of the aroma compound, limonene, as compared to oriented polypropylene (uniaxial and biaxial). The authors suggested that the interlamellar amorphous regions in the oriented films were more accessible to the penetrant because of disruptions of spherulites during drawing of the film.

Multilayer coextruded films designed to meet specific requirements are also finding wide application in food packaging. For example, the excellent gas barrier characteristics of poly(vinylidene chloride) copolymer (Saran, PVDC) can be combined with the desirable heat sealability and strength of polyolefins such as polyethylene or polypropylene. An important characteristic of multilayer films is the improvement of "dynamic" barrier properties, which provide resistance to pinholes and cracks upon abuse; multilayers tend to randomize flaws and maintain barrier characteristics (*7*). Schrenk (*7*) indicated that the oxygen permeability coefficient may be influenced by layer dimensions, which may be due to migration of plasticizer compounds to the interfaces. Liu et al. (*4*) investigated the effect of water activity on the permeation of toluene through a two-side PVDC-coated opaque OPP film and found that toluene was more effective than water vapor in promoting chain relaxation of the PVDC coating. The authors observed that at low toluene concentrations, increased water activity resulted in increased toluene permeation. However, at high toluene concentrations the effect of water activity was significantly reduced. The complex interrelationship observed between the barrier properties of the polymer, penetrant vapor activity, and sorbed water

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concentration may also apply to the permeation of other aroma compounds through films. Relative humidity (RH) and temperature were shown to strongly influence the permeation of *d*-limonene through ethylene vinyl alcohol copolymers (EVOH) and nylon 6,6 films (*8*).

Plastic packaging films are often extensively printed for marketing purposes and to provide content information and instructions. The permeability of packaging films to oxygen, moisture, and aromas may be affected by the ink system applied during the printing process, which could in turn have an impact on the quality of food within the package. Typical printing inks contain a mixture of pigments, resinous components, solvents, and plasticizers (*9*). During printing, a film is usually coated with an ink system containing a high concentration of solvent, followed by exposure to heat for removal of the solvent.

The objective of the present study was to examine the impact of printing on the permeability of selected polypropylene packaging films. OPP and coated OPP (acrylic/OPP/PVDC) films printed with commercial inks were considered. The permeations of oxygen, water vapor, and an aroma compound (*d*-limonene) were evaluated and compared.

MATERIALS AND METHODS

Materials. Biaxially oriented polypropylene films were provided by Mobil Chemical Co. (Rochester, NY) and included Bicor 100 SPW, a coextruded OPP film, 25 μm thick, flame-treated on one side and with a polyolefin sealant layer on the other side; and Bicor 318 ASB, a two-side coated OPP film, 22 μm thick, with an acrylic coating on one side and a sealable PVDC coating on the other side. Coatings were estimated by the manufacturer to be <0.05 mil (1.3 μm) thick. Films from two different production rolls were obtained to provide replicate samples. Limonene (97% pure *d*-limonene) was obtained from Sigma Chemical Co. (St. Louis, MO) and was used as received. Two commercially available inks provided by Zeneca Speciality Inks (Brampton, ON) were used for printing the OPP films. Both inks are commonly employed for flexographic and rotogravure printing of flexible food packaging: Thermosurf 50620F is a heat-resistant nitrocellulose-based ink, and Ultrabond 51612F is a polyamide-based ink. Ink "viscosity", determined using printing industry methodology, was adjusted to 25 s measured with a no. 2 Zahn cup, using a solvent mixture of 90% anhydrous ethanol and 10% *n*-propyl acetate.

Film Printing. A control coater (model 40561, R.K. Print-Coat Instruments Ltd., Herts, U.K.) equipped with a no. 2 draw bar was used to apply an ink layer (6 μm thick) on the film surface. Each printed sample was inspected visually for uniformity of the ink layer applied. Following typical industry procedures, Ultrabond ink was applied to the treated side of the SPW film and to the PVDC side of the ASB film. Thermosurf ink was also applied to the treated side of the SPW film but to the acrylic side of the ASB film. Immediately after ink application, the printed films were dried for 8 min at 90 °C in an air-circulating oven to remove solvents. Printed and unprinted (control) film samples were cut to size (9 cm × 18 cm) and a label attached to one edge of each sample. All samples were stored in a ventilated still-air oven at 40 °C until required for evaluation; these conditions were chosen to simulate extreme warehouse storage conditions for commercially printed films. A clip placed on the labeled edge was used to hang each sample from hooks on the oven racks to permit air circulation and minimize contact between samples.

Water Vapor Transmission Rate (WVTR). A two-cell Permatran-W 3/31 (Modern Controls Inc., Minneapolis, MN) was used to measure WVTR through the films. Each test cell consisted of two chambers separated by the flat film sample to be tested; one chamber was flushed with dry nitrogen and the other chamber with air saturated with water vapor. A
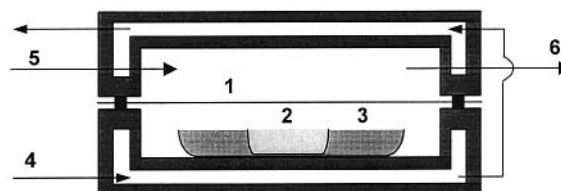

Figure 1. Schematic diagram of permeability cell used to evaluate limonene permeation through films: (1) test film; (2) water; (3) limonene; (4) circulating water bath; (5) N$_2$ gas intake; (6) carrier gas exit to GC.

sponge saturated with distilled water was placed in the wet chamber to provide 100% RH conditions. Water vapor permeating through the film sample to the dry chamber was carried by the nitrogen to an infrared detector.

WVTR measurements for all film samples were carried out at 25 and 35 °C and 100% RH. Before each measurement, samples were conditioned for 1 h at the specific testing conditions. WVTR was measured for vapor flow in both directions through control and printed films, in separate tests but using the same film sample to test the two sides, to determine whether there was a directional influence on water vapor permeation. For the ASB control film, the acrylic side was first exposed to water vapor and then the PVDC side; for the SPW control film, the treated side was first exposed to water vapor and then the sealant side. For printed films, the printed side was first exposed to water vapor and then the nonprinted side. WVTR values were recorded after 12 h, which ensured that steady state conditions were established for at least 6 h. To determine whether the WVTR remained stable over time, measurements were carried out at 4, 8, and 12 weeks after printing, using a new set of duplicate samples (single determinations of replicate samples) each time from the specific printed film group. WVTR measurements of the unprinted control films were carried out at the beginning of the experiment and at week 12, also using a new set of duplicate samples each time.

Oxygen Transmission Rate (OTR). The OTR through the films was measured using a continuous flow technique with a two-cell Ox-Tran 2/20 (Modern Controls Inc.). OTR was determined at 80% RH and at temperatures of 25 and 35 °C for the ASB films and 25 °C for the SPW films. Both up- and downstream sides of the film were maintained at the same RH, controlled by the RH option of the instrument. Duplicate film samples were removed from the storage oven and conditioned for 1 h at the corresponding temperature and relative humidity before each measurement. During conditioning, nitrogen gas was flushed over both film surfaces for 1 h to remove traces of oxygen in the sample. The stream of nitrogen on one side was then replaced by air; the nitrogen flow on the other side carried any oxygen that diffused through the film to the oxygen sensor.

OTR measurements followed a procedure similar to that outlined for WVTR. The OTR of each side of the control (unprinted) and printed samples was measured by changing the direction of air flow through each film sample to determine whether there was a directional influence on oxygen permeation. For the ASB control film, the acrylic side was first exposed to air and then the PVDC side; for the SPW control film, the treated side was first exposed to air. For all printed films, the printed side was first exposed to air, then the nonprinted side. In each case the OTR was recorded after 12 h to ensure that steady state conditions had been established for at least 6 h. Measurements were carried out at 4, 8, and 12 weeks after printing to determine whether the OTR remained stable over a 3-month period.

Limonene Permeation. The permeation of limonene through the coated OPP film (ASB) was measured using a permeability cell (Figure 1) attached to a gas chromatograph (GC) as described previously by Lim and Tung (*10*). The cell consisted of an upper and lower chamber separated by the test film sample. Complete separation and closure of each chamber were accomplished with Viton O-rings placed between the film

Printed and Unprinted Polypropylene Films

J. Agric. Food Chem., Vol. 49, No. 6, 2001 **3043**

and matching circular channels on the contact surfaces of the chambers. A circulating water jacket at 35 °C ($\pm$0.5 °C) maintained the testing temperature within the permeability cell. Limonene was placed in a glass dish (6 cm diameter, 1.5 cm height) at the bottom of the lower cell. To establish 100% RH conditions, a smaller dish (2 cm $\times$ 1.5 cm) filled with distilled water was placed in the center of the limonene dish. Limonene vapor that diffused through the film was purged by a stream of nitrogen, which flowed through the upper cell at a constant rate of 30 mL/min, and carried the permeated vapor to the GC for measurement. The GC (model 6890, Hewlett-Packard Co., Avondale, PA) was equipped with a flame ionization detector and HP3365 Chemstation software for data integration and fitted with an empty stainless steel column, 30 cm $\times$ 0.33 cm i.d. The operating conditions were as follows: oven temperature, 150 °C; detector temperature, 275 °C; N_2 flow rate, 30 mL/min; and air flow rate, 240 mL/min. A standard curve of response versus pure limonene vapor concentration was obtained by substituting the permeability cell with a glass calibration tube (8 cm $\times$ 0.7 cm o.d.) connected between the nitrogen gas inlet and the GC (Figure 1). During calibration a filter paper strip (Whatman no. 1; 1.5 cm $\times$ 0.3 cm) impregnated with a known amount of limonene was placed in the calibration tube. The limonene was vaporized and purged to the GC, yielding a standard response.

Limonene permeation was measured through control and printed ASB film samples stored at 40 °C for 8 weeks. Permeation through the nonprinted side of the printed film and both sides of the control film was measured in separate tests. Each film sample was conditioned for 1 h at 35 °C and 100% RH before exposure to limonene, and the permeation test was continued until a steady state was reached. Measurements were carried out on duplicate film samples for each side evaluated.

Film Microstructure. Scanning electron microscopy was used to observe cross sections of control and printed ASB films. Printed films were exposed to limonene vapor for 10 h at 35 °C and 100% RH, whereas the control film was not exposed to limonene. Film samples were frozen in liquid nitrogen and cross sections prepared by cutting the films with a razor blade. Samples were then mounted vertically on stubs to observe film layers and treatment effects. An SP2000A cryopreparation unit (Emscope, Ashford, Kent, U.K.) was used to prepare the samples. To avoid limonene desorption, the film samples were plunged into nitrogen slush at −207 °C, transferred under vacuum to the preparation chamber, sublimated for 20 min at −80 °C, and sputter coated with 30 nm of gold at −165 °C. The specimens were scanned using an S-570 SEM (Hitachi Ltd., Tokyo, Japan) with a beam voltage of 10 kV on a cold stage set below −130 °C.

Statistical Analyses. Analysis of variance was used to evaluate the extent to which inks affected water vapor and oxygen transmission rates through the polypropylene films. A factorial design was considered to test the effects of ink, temperature, and storage time, as well as interactions among these factors. Differences among factors and their interactions were considered to be statistically significant using a 95% confidence level. Water vapor transmission response was transformed logarithmically to normalize its distribution; therefore, mean values for WVTR are shown with their respective confidence intervals (95% CI). OTR response was not transformed; therefore, mean values are shown with standard errors. SAS/STAT 6.04 software (SAS Institute, Inc., Cary, NC) was employed for these ANOVA analyses.

RESULTS AND DISCUSSION

Water Vapor Transmission in OPP (SPW). As shown in Tables 1 and 2, printing SPW film with Thermosurf ink had some small but statistically significant influence on WVTR values as compared to unprinted control film, at both 25 and 35 °C. The Ultrabond ink had no effect ($p > 0.05$) on the WVTR of the SPW film at the conditions studied. WVTR values

Table 1. Water Vapor Transmission Rate (WVTR) of OPP Film (SPW) Printed with Thermosurf and Ultrabond Inks Tested at 25 °C and 100% RH over 12 Weeks

time (weeks)	WVTR[a] (g/m²·day)			
	Thermosurf/SPW		Ultrabond/SPW	
4	2.22[b]	2.15−2.26[b]	2.14[ab]	2.09−2.20
8	2.31[b]	2.26−2.36	2.09[a]	2.06−2.14
12	2.18[b]	2.14−2.23	2.12[ab]	2.09−2.17
control[c]	2.07[a]	2.01−2.14	2.07[a]	2.01−2.14

[a] Mean values in columns and rows sharing the same superscript letter (lowercase) are not significantly different ($p > 0.05$; $n = 96$). [b] 95% confidence intervals. [c] Mean value for control (unprinted) film was obtained from tests at weeks 0 and 12.

Table 2. Water Vapor Transmission Rate (WVTR) of OPP Film (SPW) Printed with Thermosurf and Ultrabond Inks Tested at 35 °C and 100% RH over 12 Weeks

time (weeks)	WVTR[a] (g/m²·day)			
	Thermosurf/SPW		Ultrabond/SPW	
4	5.16[abc]	4.99−5.35[b]	4.99[ab]	4.82−5.16
8	5.33[c]	5.21−5.47	4.98[a]	4.85−5.08
12	5.20[bc]	5.08−5.33	4.94[a]	4.83−5.07
control[c]	4.84[a]	4.63−5.05	4.84[a]	4.63−5.05

[a] Mean values in columns and rows sharing the same superscript letter are not significantly different ($p > 0.05$; $n = 96$). [b] 95% confidence intervals. [c] Mean value for control (unprinted) film was obtained from tests at weeks 0 and 12.

Table 3. Oxygen Transmission Rate (OTR) of OPP Film (SPW) Printed with Thermosurf and Ultrabond Inks Tested at 25 °C and 80% RH over 12 Weeks[a]

time (weeks)	OTR (mL/m²·day)	
	Thermosurf/SPW	Ultrabond/SPW
4	344.5 ± 1.0[cb]	354.7 ± 1.0[d]
8	333.2 ± 0.8[b]	342.5 ± 0.8[c]
12	324.9 ± 1.0[a]	340.4 ± 1.0[c]
control[c]	350.4 ± 3.0[cd]	350.4 ± 3.0[cd]

[a] Air (0.21 atm oxygen partial pressure) was used as test gas. [b] Mean values ± standard error; mean values in columns and rows sharing the same superscript letter are not significantly different ($p > 0.05$; $n = 32$). [c] Mean value for control (unprinted) film was obtained from tests at weeks 0 and 12.

were not significantly affected by the direction of water vapor flow through the ink layer of either printed film. OPP has a high resistance to water vapor permeation, but the hydrophilic nature of the Thermosurf ink may have resulted in an interaction between water molecules and the ink layer that enhanced the concentration-driven transport of water through the printed film structure.

Oxygen Transmission in OPP (SPW). SPW film printed with Thermosurf showed a small but significant decrease in OTR over the 12 week testing period compared to the control film (Table 3). There was no significant difference in OTR between the control film and the Ultrabond-printed film. The OTR behavior of the Thermosurf-printed film may be influenced by exposure to water vapor and therefore correlated with the WVTR results obtained for SPW film. Sorbed water molecules associated with the more hydrophilic Thermosurf ink on the film may have promoted a more compact polymer structure of the ink layer, which restrained the passage of oxygen. The Thermosurf ink, therefore, provided an additional barrier toward oxygen at the 80% RH conditions studied. It is possible that a secondary crystallization effect, promoted by the interaction of water and Thermosurf ink, enhanced the gas

Table 4. Oxygen Transmission Rate (OTR) of OPP Film (ASB) Printed with Thermosurf Ink Tested at 35 °C and 80% RH over 12 Weeks[a]

time (weeks)	OTR from PVDC side (mL/m²·day)	OTR from acrylic side (mL/m²·day)
4	62.2 ± 3.1^{deb}	49.4 ± 3.1^{abc}
8	52.3 ± 2.2^{bc}	46.6 ± 2.2^{a}
12	56.5 ± 2.2^{cd}	47.1 ± 2.2^{a}
control[c]	64.1 ± 1.2^{e}	46.8 ± 1.2^{a}

[a] Air (0.21 atm oxygen partial pressure) was used as test gas. [b] Mean values ± standard error; mean values in columns and rows sharing the same superscript letter are not significantly different ($p > 0.05$; $n = 94$). [c] Mean value for control (unprinted) film was obtained from tests at weeks 0 and 12.
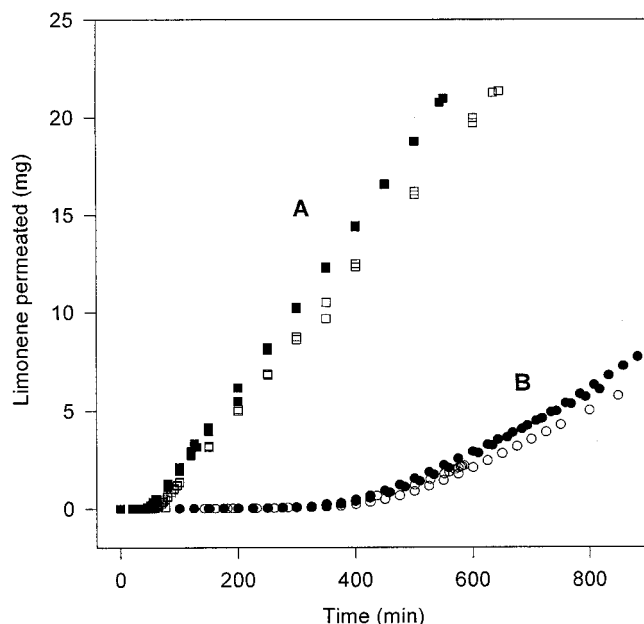

Figure 2. Permeation curves for limonene vapor through ASB films at 35 °C and 100% RH: (A) PVDC side exposed to limonene [(■) Thermosurf printed on acrylic side; (□) unprinted film]; (B) acrylic side exposed to limonene [(●) Ultrabond printed on PVDC side; (○) unprinted film].

barrier of the printed film. This hypothesis could be tested by exposing the printed film to different water activities.

A comparison of the WVTR and OTR results for the control and printed SPW films indicated that permeation could be influenced by the type, but not simply the presence, of printing ink on the film. Only the Thermosurf ink had a significant effect on increasing WVTR and reducing OTR through printed SPW films compared to unprinted control films at the conditions studied.

Water Vapor Transmission in Coated OPP (ASB). WVTR values obtained for all unprinted and printed ASB films were not significantly different ($p > 0.05$) and did not change over the 12 week period studied. Therefore, neither the presence nor the type of ink appeared to have an influence on WVTR of these coated films.

Oxygen Transmission in Coated OPP (ASB). No significant differences ($p > 0.05$) in OTR were found between the control and all printed ASB films at 25 °C and 80% RH or between the control and Ultrabond-printed ASB films at 35 °C and 80% RH. At 35 °C, however, the OTR of Thermosurf-printed ASB films decreased slightly over time compared to the control film, when oxygen was exposed to the PVDC side (Table
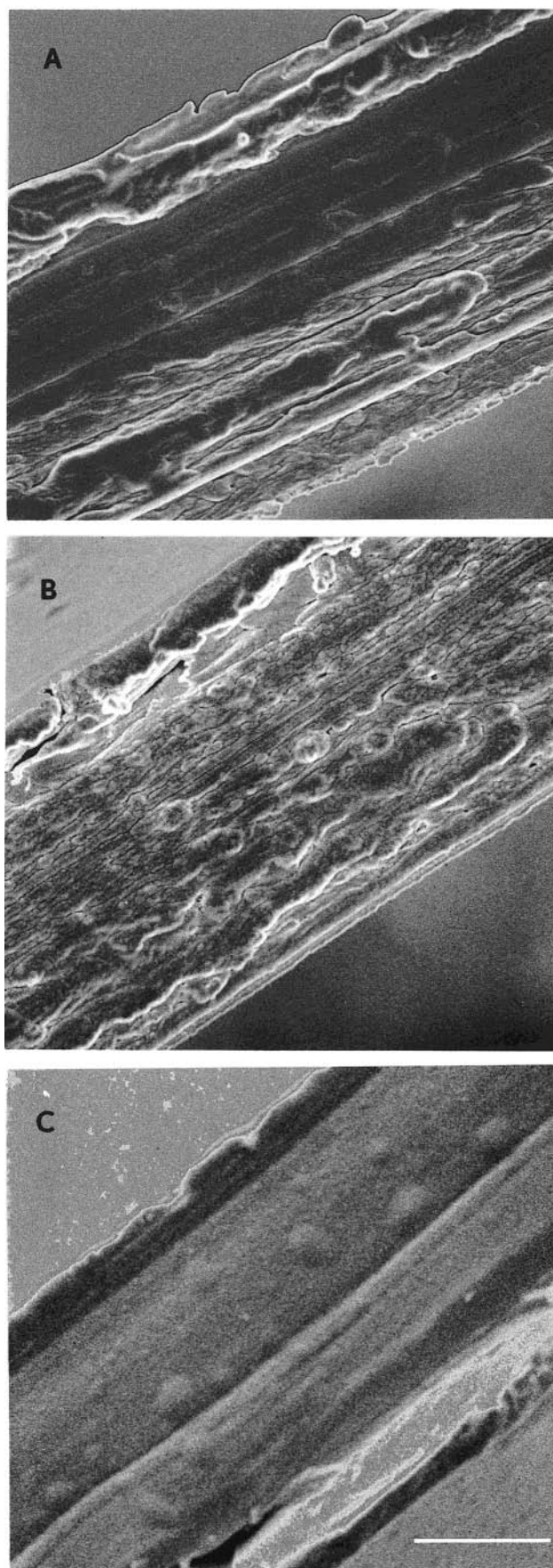

Figure 3. SEM of cross sections of printed ASB films exposed to limonene and control ASB film: (A) printed [Ultrabond ink (top), PVDC, OPP, acrylic layer (bottom)]; (B) printed [Thermosurf ink (top), acrylic, OPP, PVDC (bottom)]; (C) control [acrylic layer (top), OPP, PVDC (bottom)]. Bar is 10 μm.

Printed and Unprinted Polypropylene Films

J. Agric. Food Chem., Vol. 49, No. 6, 2001 **3045**

4). Also, at each of the time periods measured, the OTR from the PVDC side of the ASB film was significantly higher than the corresponding OTR from the acrylic side, in both the printed and unprinted films. These results suggested that the barrier properties imparted by the film coatings were more important in oxygen transmission than the presence or type of ink.

As expected, the coatings in the ASB film provided an improved oxygen barrier as compared to the SPW film; however, the directional influence observed for OTR at 35 °C suggests some interaction between water molecules and the PVDC side of the film. Liu et al. (*4*) proposed that the amount of sorbed water and its effect on the barrier characteristics of PVDC may be dependent upon the resin formulation and preparation of the PVDC copolymer. The PVDC used for coating OPP would be expected to have a different formulation than a PVDC barrier film, and likely be more sensitive to moisture.

Limonene Permeation in Coated OPP (ASB). In this study only the nonprinted side of the ASB film was exposed to the aroma compound, because a packaged food product containing aroma compounds would be in direct contact with only the nonprinted side of the package. A comparison of curves A and B in Figure 2 illustrates how the permeation of limonene through control and printed ASB films at 35 °C and 100% RH was markedly influenced by the film coating (or layer) exposed to the aroma compound. The ASB film provided a substantially better aroma barrier when the acrylic side of the film was exposed to limonene. Both inks had only a minor effect on limonene permeation, compared to the effect of the coatings. One possible explanation for the striking effect of the coatings is that an interaction between the limonene and the PVDC coating may be associated with a relaxation of the polymeric structure, thereby permitting additional penetrant sorption and increased limonene permeation. Liu et al. (*4*) described a similar interaction for toluene vapor permeation through PVDC-coated OPP and hypothesized that both water vapor and toluene interacted more with the PVDC coating than with the OPP film. An alternate explanation is that the PVDC coating could act as a sponge for limonene at the PP surface, which sets up a concentration differential between the PP sides that favors the aroma transfer.

Film Microstructure. Scanning electron micrographs of cross sections of the ASB films revealed that the PVDC and acrylic coatings of both printed films exposed to limonene exhibited swelling and some stratification (Figure 3A,B) as compared to the intact coatings of the unexposed control film (Figure 3C). The OPP structure (middle) of the printed films exhibited a spongelike appearance with stratifications and small channels, compared to the compact OPP structure of the control film. More compact areas were apparent in the OPP structure of the Ultrabond-printed film (Figure 3A) than in the Thermosurf-printed film (Figure 3B) and may be correlated to which film coating was exposed to

limonene. The Thermosurf-printed film was exposed to limonene from the PVDC side, which may have allowed for an interaction between limonene and the PVDC, resulting in a greater relaxation of the compact polymer structure.

LITERATURE CITED

(1) Smith, J. S.; Peppas, N. A. Mathematical analysis of transport properties of polymer films for food packaging. VII. Moisture transport through a polymer film with subsequent adsorption on and diffusion through food. *J. Appl. Polym. Sci.* **1991**, *43*, 1219−1225.

(2) Letinski, J.; Halek, G. W. Interactions of citrus flavor compounds with polypropylene films of varying crystallinities. *J. Food Sci.* **1992**, *57*, 481−484.

(3) Stern, S. A.; Trohalaki, S. Fundamentals of gas diffusion in rubbery and glassy polymers. In *Barrier Polymers and Structures*; Koros, W. J., Ed.; ACS Symposium Series 423; American Chemical Society: Washington, DC, 1990; pp 22−59.

(4) Liu, K. J.; Hernandez, R. J.; Giacin, J. R. The effect of water activity and penetrant vapor activity on the permeation of toluene vapor through a two-side PVDC coated opaque oriented polypropylene film. *J. Plastic Film Sheeting* **1991**, *7*, 56−67.

(5) Taraiya, A. K.; Orchard, G. A. J.; Ward, I. M. The effect of amorphous orientation on the oxygen permeability of polypropylene films. *J. Polym. Sci. Part B: Polym. Phys.* **1993**, *31*, 641−645.

(6) Moaddeb, M.; Koros, W. J. Effects of orientation on the transport of *d*-limonene in polypropylene. *J. Appl. Polym. Sci.* **1995**, *57*, 687−703.

(7) Schrenk, W. J. Multilayer plastic films. In *Technological Aspects of the Mechanical Behavior of Polymers*; Boyer, R. F., Ed.; Applied Polymer Symposia 24; Wiley: New York, 1974; pp 9−12.

(8) Zhang, Z.; Lim, L.-T.; Tung, M. A. Limonene transport and mechanical properties of EVOH and nylon 6,6 films as influenced by RH. *J. Appl. Polym. Sci.* **2000**, *79*, 1949−1957.

(9) Soroka, W. Package printing and decoration. In *Fundamentals of Packaging Technology*; Institute of Packaging Professionals: Herndon, VA, 1995; pp 85−110.

(10) Lim, L.-T.; Tung, M. A. Vapor pressure of allyl isothiocyanate and its transport in PVDC/PVC copolymer packaging film. *J. Food Sci.* **1997**, *62*, 1061−1066.